THE JOURNAL

OF THE

AMERICAN LEATHER CHEMISTS ASSOCIATION

VOL. XLIX APRIL 1954 No. 4

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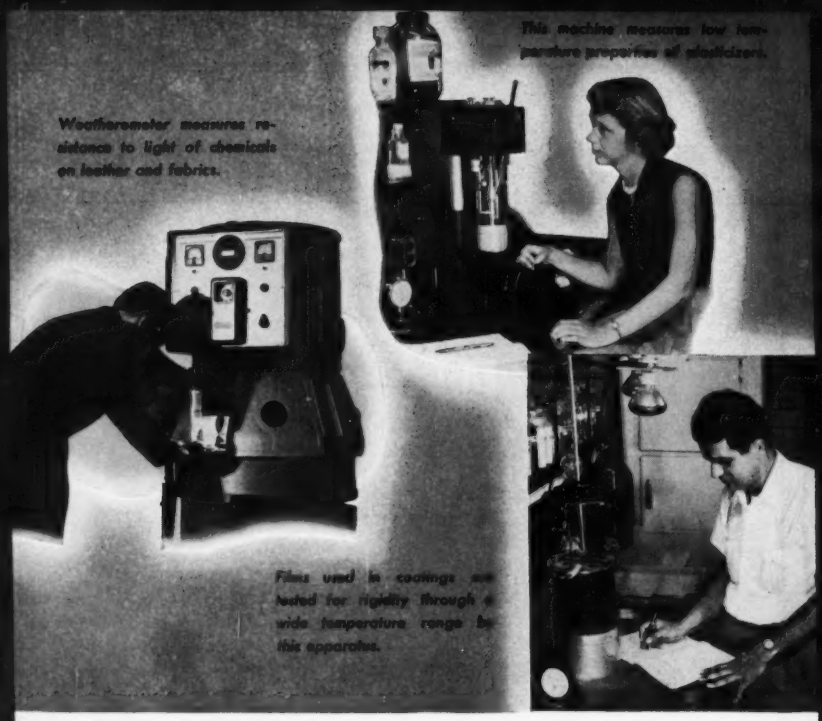
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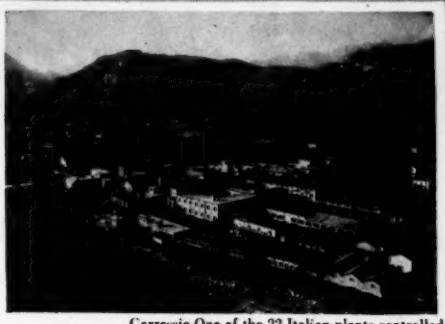

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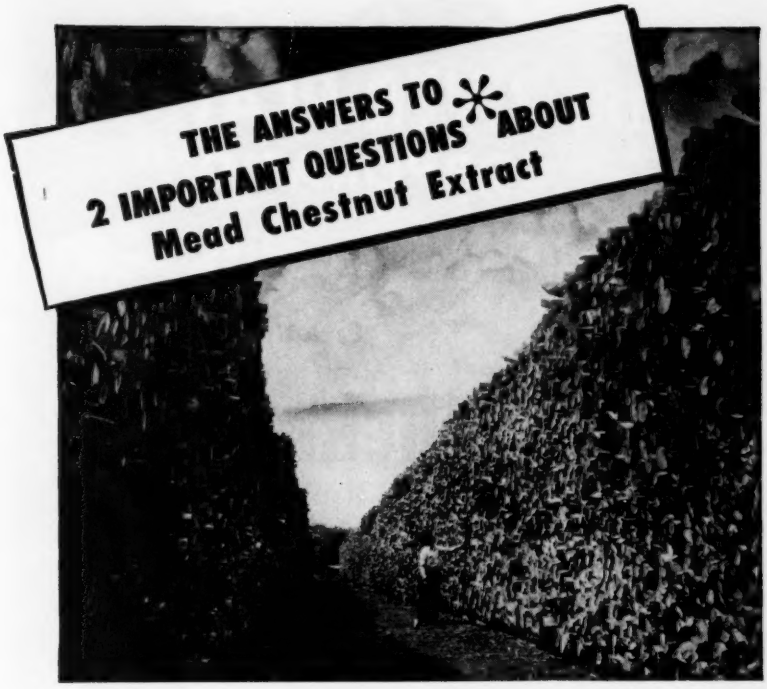

This is only a portion of the many stockpiles of chestnut logs that insure a continuous supply of Chestnut Extract.

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B. Since the tanning system demands acid, the use of chestnut, with its plumping acidity, saves you money.

C. Mead Chestnut Extract eliminates up to 28% of leachhouse losses.

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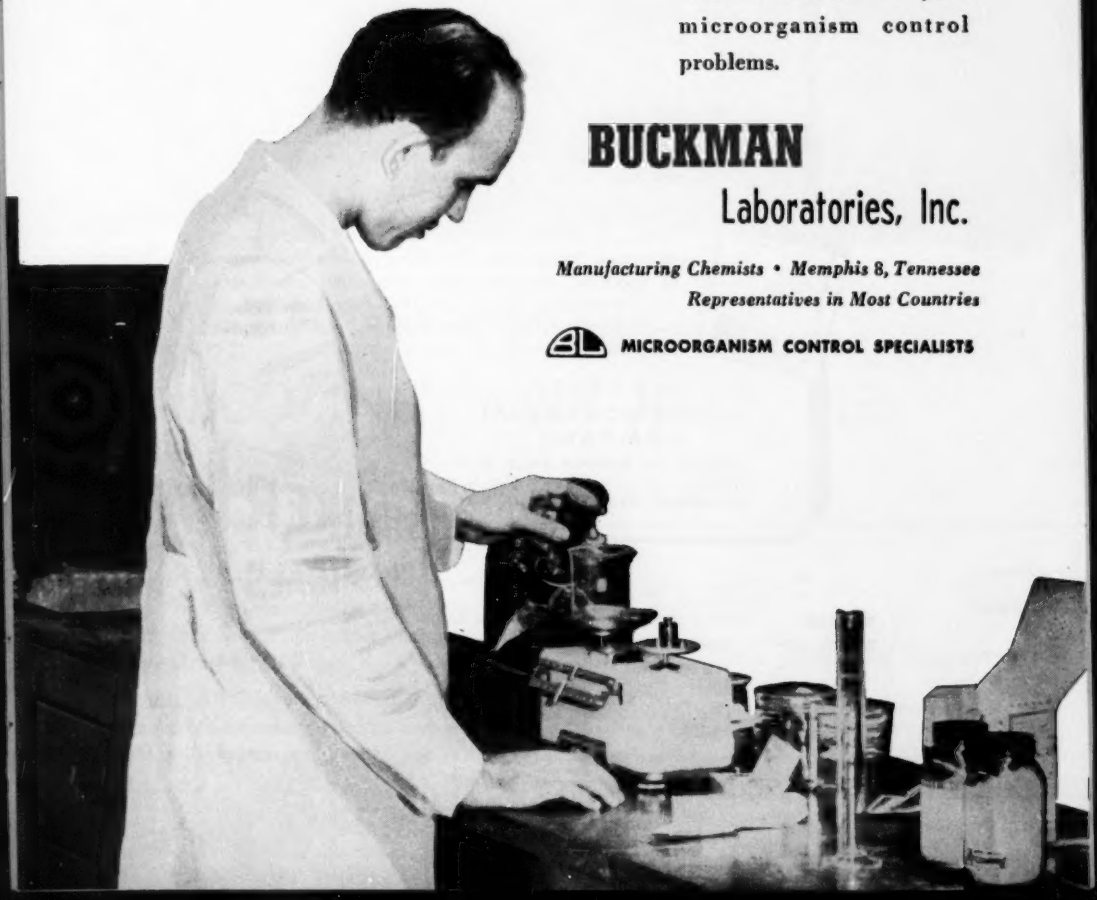

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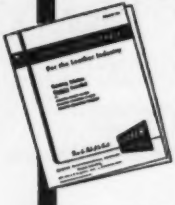

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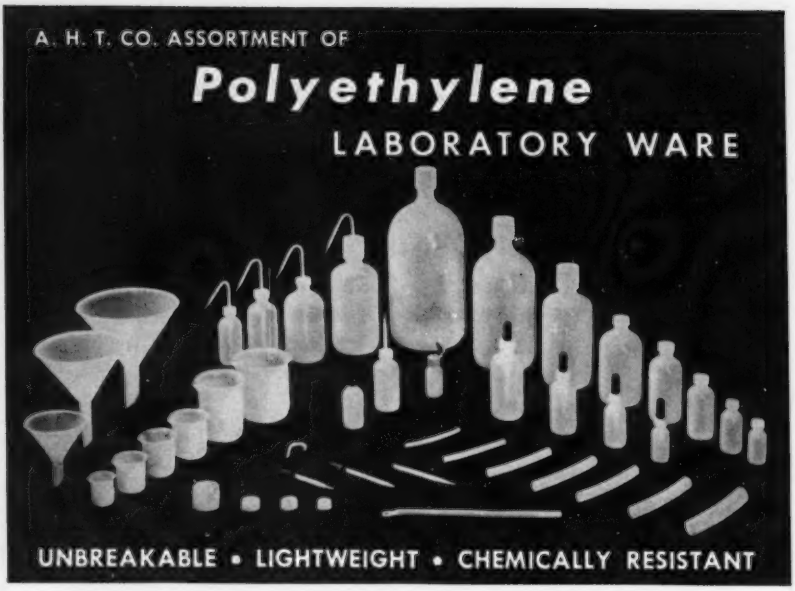

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METHOD FOR COPPER AND IRON IN TANNING MATERIALS (A31)

1. SCOPE

1.1 This method is intended for use in determining iron and copper in vegetable tanning materials. It is applicable to liquid, solid, pasty and powdered extracts, to raw and spent materials, and to tannery liquors.

2. SAMPLE AND SPECIMEN

2.1 The sample shall be taken as described in Method J10.

2.2 The specimen shall consist of 5 g. of solid extract or its equivalent (i. e. 10 g. of liquid extract; 5 g. of raw and spent materials; 25-50 g. of tannery liquor), prepared as described in Method J10, except in the case of raw and spent materials which shall be prepared as in Method A5, par. 2.1.

3. APPARATUS AND REAGENTS

3.1 Matched Nessler tubes and supporting rack. (See also par. 4.5.)

3.2 Concentrated Sulfuric Acid: 96 per cent.

3.3 Sulfuric Acid solution: concentrated, diluted 1:20 with distilled water.

3.4 Fuming Nitric Acid.

3.5 Concentrated Hydrochloric Acid: 36 per cent.

3.6 Hydrochloric Acid solution: 1.0 normal.

3.7 Bromine Water: saturated solution.

3.8 Ammonium hydroxide solution: concentrated, diluted 1:1 with distilled water.

3.9 Potassium permanganate solution: 0.1 normal.

3.10 Potassium (or Ammonium) thiocyanate solution: 10 g. shall be dissolved in distilled water and diluted to 100 ml. with distilled water.

3.11 Stock Iron Solution: This may be purchased "Iron Standard" solution or may be prepared as follows: 0.70 g. of crystallized ferrous ammonium sulfate $FeSO_4.(NH_4)_2SO_4.6H_2O$ shall be dissolved in 50 ml. of distilled water and 20 ml. of dilute sulfuric acid (1:4). The solution shall be titrated with 0.1 *N* potassium permanganate solution until a faint pink persists for 1 minute and the iron is completely oxidized. Dilute to 1 liter with distilled water. 1 ml. of this solution is equivalent to 0.0001 g. Fe. The solution shall be stored in brown bottles and be protected from light.

3.11.1 Standard Iron solution: 10 ml. of the prepared stock solution, or its equivalent of purchased "Iron Standard" (par. 3.11), shall be diluted to 100 ml. with distilled water. 1 ml. of this standard solution is equivalent to 0.00001 g. Fe. The standard solution shall be freshly prepared.

3.12 Stock Copper solution: 3.9283 g. of copper sulfate crystals ($CuSO_4 \cdot 5H_2O$) shall be dissolved in distilled water and diluted to 1 liter with distilled water. 1 ml. of this solution is equivalent to 0.001 g. Cu.

3.12.1 Standard Copper solution: 10 ml. of the stock solution (par. 3.12) shall be diluted to 1 liter with distilled water and the pH adjusted to between 5.5 and 6.0. 1 ml. of this standard solution is equivalent to 0.00001 g. Cu. The standard solution shall be freshly prepared.

3.13 Xanthate solution: 1.0 g. of potassium ethyl xanthate shall be dissolved in distilled water and diluted to 1 liter with distilled water. The solution shall be freshly prepared.

4. GENERAL

4.1 The distilled water shall have been distilled from a tin-lined, block tin, or glass still and shall be stored in tin-lined, block tin, or glass containers.

4.2 All apparatus shall be cleaned with hot hydrochloric acid solution (1:1) and rinsed with distilled water before use.

4.3 Blank determinations shall be made to minimize errors due to iron or copper either present in the reagents used or picked up during the analysis.

4.4 Duplicate determinations are recommended whenever possible.

4.5 In the actual colorimetric determinations described below (pars. 5.3.1 – 5.3.4. and 5.4.1–5.4.3), the indicated volumes of reagents, and of the prepared solutions of the specimens and of the standards, are based on the use of 50 ml. tall-form, Nessler tubes. Other tube volumes and forms may be used, provided:-

A. they be used in matched sets,

B. the volumes of reagents, specimen and standard solutions be adjusted so that similar color intensities are produced. Such adjustments are automatic with, and familiar to, the experienced analyst and are not precluded by the method. If, however, the analyst is in doubt as to the proper adjustments to be made, it is recommended that 50 ml., tall-form, tubes be used exactly as described.

4.6 Comparison of the colors developed in the Nessler tubes (pars. 5.3.3 and 5.4.2) shall be made under a source of daylight from the north, the tubes being held vertically two inches above an inclined sheet of white paper, and viewed downward through the full depth of liquid.

5. PROCEDURE

5.1 The specimen shall be transferred to a tared, glazed, porcelain dish or crucible of suitable size, taking care to avoid changes in moisture content, and weighed to the nearest 0.1 mg. Where necessary, the dish and specimen shall be placed in the oven (Method A13) and evaporated to dryness.

5.2 The dish containing the dried residue shall be ignited gently over a low flame, at as low a temperature as possible, until the residue is thoroughly charred and all smoke driven off. The dish and charred residue shall then be placed in a muffle furnace and ashed, at a temperature not exceeding 600°C, until all carbon has been removed. (Occasionally, the specimen will be of such a nature that all the carbon cannot be removed as described above. In such a case, the charred mass shall be saturated with hot distilled water and broken up as completely as possible with a glass rod. More of the hot distilled water shall then be added and the whole digested on the steam bath for a few minutes. The supernatant shall be decanted through a quantitative filter paper, the filtrate being collected in a suitable receiver. The charred residue shall be digested twice more with hot distilled water, the supernatant being decanted through the same filter each time, and the filtrates combined. Finally, the char shall be transferred to the filter and washed several times with hot distilled water—the washings being combined with the filtrates. The filter and residue shall then be replaced in the original dish, dried, and the whole ashed, as before, until all carbon has been removed. The dish shall be cooled, the combined filtrates and washings quantitatively transferred thereto and evaporated and dried. The dish and contents shall then be placed in a cold muffle, the temperature raised, slowly at first to avoid loss by spurting, and finally brought to a value not exceeding 600° C.)

5.2.1 The carbon-free ash shall be cooled, moistened with hot distilled water, 5 ml. of concentrated hydrochloric acid added, and the mixture heated on the steam bath until the ash is dissolved. 5 drops of fuming nitric acid and 5 drops of bromine water shall then be added and the mixture heated on the steam bath, gently at first until evolution of gas ceases (use fume cupboard or hood), and finally evaporated to dryness. The residue shall then be moistened with distilled water, 5 ml. of concentrated hydrochloric acid added, the mixture digested on the steam bath for a few minutes and finally transferred, quantitatively, into a 250 ml. beaker. The volume shall be adjusted to about 75 ml. by boiling if necessary. The solution shall then be made faintly ammoniacal with ammonium hydroxide solution (1:1) and boiled gently to remove excess ammonia and to coagulate the precipitated iron and aluminum hydroxides.

5.2.2 The mixture shall then be allowed to stand on the hot plate, for a few minutes, until the precipitate has settled. As soon as possible thereafter, the hot supernatant shall be decanted through a suitable filter paper except when copper is to be determined, in which case an asbestos-gooch filter (previously washed with hot, 1:1, hydrochloric acid, distilled water, 1:1 ammonium hydroxide, and distilled water) shall be used (ammoniacal copper solutions combine with cellulose.) The precipitate shall be washed three times, by decantation, with hot, faintly ammoniacal, distilled water (5 drops 1:1 ammonium hydroxide solution per liter). Finally, the precipitate shall be quantitatively

transferred to the filter and washed four times with the hot, faintly ammoniacal distilled water. The residue on the filter shall be reserved for the determination of iron (par. 5.3 below), and the combined filtrate and washings reserved for the determination of copper (par. 5.4 below).

5.3 *Iron.* The residue on the filter shall be dissolved by running onto it two portions of 1:20 sulfuric acid solution, of 20 ml. each, the solution being collected in a suitable receiver. The filter shall then be thoroughly washed, four times, with 1:20 sulfuric acid solution, the washings being added to the first 40 ml. The combined acid solution and washings shall be quantitatively transferred to a suitable volumetric flash (usually 200 ml. is adequate), cooled if necessary, and brought to the mark with 1:20 sulfuric acid solution. A quantitative test of this solution should be made as a guide to the proper size of aliquot required in the quantitative determination below.

5.3.1 To the known aliquot of the above solution in a Nessler tube, shall be added sufficient 1:20 sulfuric acid solution to bring to a volume of 35 ml., two drops of 0.1 *N* potassium permanganate solution, and the contents of the tube mixed and then allowed to stand for 5 minutes, more permanganate solution being added, if necessary, until a slight pink persists. (Where several specimens are being examined, all the specimen tubes shall be prepared, as above, at the same time.

5.3.2 A series of standard Nessler tubes shall be similarly prepared, containing 0.5–1.5 ml. of standard iron solution (par. 3.11.1) in increments of 0.1 or 0.2 ml., the iron solution being added from a burette. The contents of the tubes shall be mixed and then allowed to stand for 5 minutes, more permanganate solution being added, if necessary, until a slight pink persists.

5.3.3 To each of the specimen and standard tubes 5 ml. of 10 per cent thiocyanate solution shall then be added, immediately followed by sufficient distilled water to bring to the mark, and the contents of each tube shall be thoroughly mixed by inverting the tube several times. The color of the specimen tube shall be compared immediately with that of the standards. The volume of standard iron solution in that standard (or estimate) whose color most closely matches that of the specimen shall be recorded. (With care, the color can be estimated to 0.05 ml.)

5.3.4 If the color of the specimen tube be outside the range of the standards, the comparison shall be repeated with fresh standards and an aliquot of more suitable size.

5.4 *Copper.* The pH of the combined ammoniacal filtrate and washings from Par. 5.2.2 shall be adjusted to between 5.5 and 6.0 by careful addition of 1.0 *N* hydrochloric acid. The adjusted solution shall then be quantitatively transferred to a suitable volumetric flask (250 ml. is usually adequate), cooled if necessary, and brought to volume with distilled water.

5.4.1 A series of standard Nessler tubes shall be prepared containing 0–4 ml. of standard copper solution (par. 3.12.1) in 0.5 ml. increments, the

copper solution being added from a burette. To each standard tube, 10 ml. xanthate solution (par. 3.13) shall be added and sufficient distilled water to bring to volume. The contents of the tubes shall then be thoroughly mixed by inverting several times.

5.4.2 To another Nessler tube shall be added a known aliquot of the solution prepared as in par. 5.4, followed by 10 ml. of xanthate solution and sufficient distilled water to bring to volume. The contents of the tube shall be thoroughly mixed by inverting several times, and the color compared with that of the standards. The comparison shall be made within 15 minutes of the addition of xanthate to the specimen and standard tubes. The volume of standard copper solution in that standard whose color most closely matches that of the specimen tube shall be recorded. (With care, the color can be estimated to the equivalent of 0.25 ml. of standard copper solution.)

5.4.3 If the color of the specimen tube be deeper than that of the 4.0 ml. standard, the comparison shall be repeated using a lesser aliquot.

6. RESULTS

6.1 *Iron.* Results may be expressed as parts per million or as per cent iron as Fe, whichever is preferred. The iron content of the sample shall equal:

$$\frac{(m - b) \times v}{1000 \times q \times w} \quad \text{per cent as Fe}$$

Where: m = ml. of standard iron solution in matching standard.
v = capacity (ml.) of the volumetric flask (usually 200 ml.) used in par. 5.3.
q = aliquot (ml.) taken in par. 5.3.1.
b = ml. of standard iron solution matching q ml. of blank.
w = g. of specimen (par. 2.2).

6.2 Instead of the visual color comparison, the use of a standard photelometer shall be permissible, provided the calibration curve be established on standards made up following the procedures in pars. 5.3.2 and 5.3.3. (It is advisable to recheck the calibration curve at regular intervals.) In this case, the name of the photelometer used shall be stated on the report.

6.3 *Copper.* Results may be expressed as parts per million or as per cent copper as Cu, whichever is preferred. The copper content of the sample shall equal:

$$\frac{(m - b) \times v}{1000 \times q \times w} \quad \text{per cent as Cu}$$

Where: m = ml. of standard copper solution in matching standard.
v = capacity (ml.) of the volumetric flask (usually 250 ml.) used in par. 5.4.
q = aliquot (ml.) taken in par. 5.4.2.

b = ml. of standard copper matching q ml. of blank.
w = g. of specimen (par. 2.2)

6.4 Due to a cloudiness which develops, especially in the specimen solutions, this method is not suitable for use with photelometers. This same cloudiness introduces difficulty in the visual method since it must be overlooked if reliable results are to be obtained.

A.L.C.A. Provisional Method February 1954.

SAMPLING OF BEAMHOUSE LIQUORS (J30)

1. SCOPE

1.1 These procedures are intended for use in obtaining representative samples of soak waters, lime liquors, warm water pools, bate waters and other waters found in the tannery beamhouse.

2. PROCEDURE

2.1 The liquor shall be thoroughly agitated, either by plunging or by running the paddle wheel if the vats are so equipped, to bring all solid matter into suspension. A sample volume of 1 liter shall be taken, packaging in a well-stoppered bottle and mixing thoroughly just before pipetting sample for analysis.

2.2 In certain instances, plunging may be done by air rather than by mechanical means.

2.3 Where bacterial action might proceed, as in the case of soak waters and bate waters, there shall be added, as a preservative, about 2 g. of beta-naphthol per liter of sample.

A.L.C.A. Provisional Method February 1954.

SOAK WATERS - GENERAL (F1)

1. SCOPE

1.1 This method is intended to identify the various components of a soak water that are normally scrutinized by analysis.

2. SPECIMEN

2.1 The water shall be sampled in accordance with Method J30 and the analysis, except for pH determination, shall be carried out on a filtered sample.

3. APPARATUS AND REAGENTS

3.1 All volumetric glassware, used in the chemical analysis, shall comply with the specifications for Class B of Federal Specifications DD-V-581, Volu-

metric Apparatus, Glass.

3.2 Unless otherwise specified, all reagents used in the chemical analysis shall comply with specifications recommended by the Committee on Analytical Reagents of the American Chemical Society.

3.3 The distilled water used in the chemical analysis shall have a pH of not less than 5.5 nor more than 7.0 and shall give a residue of not more than 0.0005 g. when 100 ml. are evaporated and dried in a platinum dish.

3.4 General laboratory apparatus and reagents shall be available. (Special apparatus and reagents are described in the individual methods.)

4. PROCEDURE

4.1 *Solids and Ash.* Solids and ash shall be determined as in Method F10.

4.2 *Total Nitrogen.* Total nitrogen shall be determined as in Method B5, modified to employ a liquid sample, accurately pipetted, which shall contain approximately 20 mg. of nitrogen.

4.3 *Total Volatile Nitrogen.* Total volatile nitrogen shall be determined as in Method F20.

4.4 *Volatile Amine Nitrogen and Free Ammonia Nitrogen.* The total volatile amine nitrogen and free ammonia nitrogen shall be determined as in Method F21.

4.5 *Calcium.* Calcium shall be determined as in Method F40.

4.6 *Chlorides.* The chloride or salt content of the soak water shall be determined as in Method F50.

4.7 *Sulfates.* The sulfate content shall be determined as in Method F52.

4.8 *pH Value.* The pH of the soak water shall be determined as outlined in Method F60.

A.L.C.A. Provisional Method February 1954.

LIME LIQUORS - GENERAL (F3)

1. SCOPE

1.1 This method is intended to enumerate the various components of lime liquors and warm water pools that are normally scrutinized by analysis.

2. SPECIMEN

2.1 The liquor shall be sampled as outlined in Method J30 and the analyses shall be undertaken on filtered samples, except for pH determination.

3. APPARATUS AND REAGENTS

3.1 The specifications for glassware, reagents and distilled water, required for the analyses, shall conform to Method F1 (par. 3).

4. PROCEDURE

4.1 *Solids and Ash.* Solids and ash shall be determined as in Method F10. On occasion, it may be desirable to make these determinations on the unfiltered sample also.

4.2 *Total Nitrogen.* Total nitrogen shall be determined as in Method B5, except that this method shall be modified to employ a liquid sample, accurately pipetted, which shall contain approximately 20 mg. of nitrogen.

4.3 *Total Volatile Nitrogen.* Total volatile nitrogen shall be determined as in Method F20.

4.4 *Volatile Amine Nitrogen and Free Ammonia Nitrogen.* The total volatile amine nitrogen and free ammonia nitrogen shall be determined as in Method F21.

4.5 *Total Caustic Alkalinity.* Total caustic alkalinity shall be determined as in Method F35.

4.6 *Calcium.* The lime content of the lime liquor shall be determined as in Method F40.

4.7 *Chlorides.* The salt content of the lime liquor shall be determined as in Method F50.

4.8 *Sulfides.* The sulfide content shall be determined as in Method F51.

4.9 *pH Value.* The pH of the lime liquor shall be determined as outlined in Method F60.

A.L.C.A. Provisional Method February 1954.

BATE WATERS - GENERAL (F5)

1. SCOPE

1.1 This method is intended to identify the various components of bate waters, that are normally scrutinized by analysis.

2. SPECIMEN

2.1 The bate water shall be sampled in accordance with Method J30 and the analyses shall be undertaken on filtered samples, except for pH determination.

3. APPARATUS AND REAGENTS

3.1 The specifications that shall apply for glassware, reagents and distilled water, used for the analysis, shall be as outlined in Method F1 (par. 3.).

4. PROCEDURE

4.1 *Solids and Ash.* Solids and ash shall be determined as in Method F10.

4.2 *Total Nitrogen.* Total nitrogen shall be determined as in Method B5, except that the method shall be modified to employ a liquid sample, accurately pipetted, which shall contain approximately 20 mg. of nitrogen.

4.3 *Ammonia in Bate Waters.* The free ammonia and total ammonia content of bate waters shall be determined as in Method F30.

4.4 *Calcium.* Calcium shall be determined as in Method F40.

4.5 *Chlorides.* Chlorides shall be determined as in Method F50.

4.6 *Sulfates.* Sulfates shall be determined as in Method F52.

4.7 *pH Values.* The pH of the bate water shall be determined as outlined in Method F60.

A.L.C.A. Provisional Method February 1954.

SOLIDS AND ASH OF BEAMHOUSE LIQUOR (F10)

1. SCOPE

1.1 This method is intended for use in determining the dry solids content and the ash content of beamhouse liquors.

2. SPECIMEN

2.1 The beamhouse liquors shall be sampled as described in Method J30 and, depending on the intent, the sample employed for analysis may be filtered or not filtered.

3. APPARATUS AND REAGENTS

3.1 Combined Evaporator and Dryer, as described in Method A13, par 2.1 or a Precision-Freas Mechanical Convection Oven, as described in Method. A13, par. 2.2.

3.2 Tared porcelain or platinum dish.

4. PROCEDURE

4.1 *Solids.* An accurately measured volume of beamhouse liquor, containing not more than 1 g. of dry solids, shall be pipetted into a tared porcelain or platinum dish. The dish, containing the specimen, shall be placed in the drying oven and evaporated and dried as specified in Method A13.

4.2 *Ash.* Without removing from the dish, the dried sample from the Solids determination (par. 4.1) shall be ignited beginning at a low temperature and ending at the highest temperature attainable with an ordinary Bunsen burner, allowing free access of air to the contents of the crucible during the ignition. The ash shall be cooled in a desiccator and weighed.

5. RESULTS

5.1 The solids and ash shall be reported in per cent, by volume. Depending

on whether the sample was filtered or not filtered, the solids shall be reported as Soluble Solids or Total Solids.

A.L.C.A. Provisional Method February 1954.

TOTAL VOLATILE NITROGEN (F20)

1. SCOPE

1.1 This method is intended for use in the analysis of beamhouse liquors and the term "Total Volatile Nitrogen" refers fo the sum of the free ammonia and volatile amine nitrogen.

2. SPECIMEN

2.1 The liquor shall be sampled as described in Method J30, and a measured volume for analysis shall contain 30-35 mg. of total volatile nitrogen.

3. APPARATUS AND REAGENTS

3.1 The apparatus shall be as described in Figure F20.

3.2 Standardized 0.1*N* sulfuric acid.

3.3 Phenolphthalein indicator solution, 0.5 gm. per 100 ml. 95 per cent ethyl alcohol.

3.4 Calcium hydroxide paste.

3.5 Methyl red indicator, 0.1 gm. per 100 ml. 95 per cent ethyl alcohol.

3.6 Standardized 0.1*N* sodium hydroxide.

4. PROCEDURE

4.1 A measured volume of liquor, containing 30-35 mg. of total volatile nitrogen, shall be distilled under reduced pressure in the presence of excess $Ca(OH)_2$, into a known amount of 0.1*N* H_2SO_4, in the apparatus shown in Figure F20.

4.2 A 50 ml. portion of standard acid shall be pipetted into the flasks R_1 and R_2, about one-quarter of the total amount being placed in the latter, so that the end of the side-arm tube of R_1 is well covered.

4.3 The sample shall be placed in flask D, and made alkaline to phenolphthalein with $Ca(OH)_2$ paste and the distillation shall be started and continued for 40-45 minutes using the vacuum of a good water pump. The distilling temperature shall not be higher than 60-70° C. A few drops of paraffin oil may be used to prevent foaming.

4.4 At the end of the distillation, the contents of R_1 and R_2 shall be quantitatively transferred to a 400 ml. beaker. The side-arm tube of R_1 and the tube G shall be carefully washed and the washings added to the same

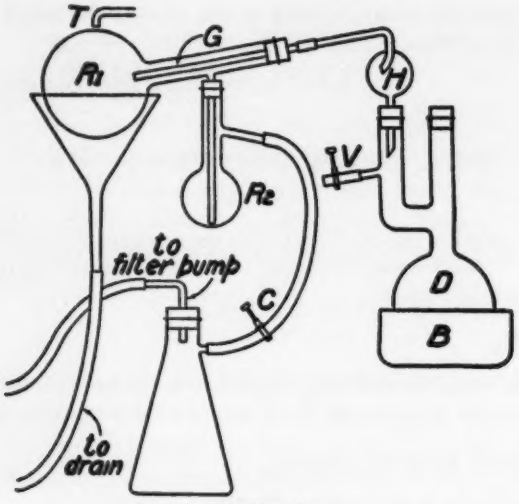

FIGURE F-20

beaker. The excess acid shall be titrated with 0.1*N* NaOH, using brom cresol green or methyl red as the indicator.

4.5 The titrated distillate shall be used for the separation of total volatile amine nitrogen and free ammonia nitrogen as described in Method F21.

5. RESULTS

5.1 The percentage of nitrogen shall be calculated from the ml. of 0.1*N* acid neutralized by the ammonia distillate as follows:

$$\text{Per cent nitrogen} = \frac{\text{ml. of } 0.1N \text{ acid} \times 14 \times 100}{\text{volume of specimen}}$$

5.2 The total volatile nitrogen shall be reported in per cent by volume.

A.L.C.A. Provisional Method February 1954.

TOTAL VOLATILE AMINE NITROGEN AND FREE AMMONIA NITROGEN (F21)

1. SCOPE

1.1 This method is intended for the separation of the free ammonia nitrogen from the volatile amine nitrogen in soak waters and lime liquors.

2. SPECIMEN

2.1 The sample employed shall be the titrated distillate from the total volatile nitrogen determination in Method F20.

3. APPARATUS AND REAGENTS

3.1 The apparatus shall be as described in Figure F21.

3.2 Solution composed of equal parts of 20 per cent sodium hydroxide and 30 per cent sodium carbonate solutions.

3.3 Powdered mercuric oxide, yellow.

3.4 Soltuion composed of 22.7 gm. mercuric iodide, 33.0 gm. of potassium iodide and 35.0 gm. sodium hydroxide in 1000 ml.

4. PROCEDURE

4.1 The titrated distillate from Method F20 shall be transferred to a 500 ml. volumetric flask, diluted to 480 ml. of 10 ml. of a solution composed of equal parts of 20 per cent NaOH and 30 per cent Na_2CO_3 solutions shall be added. The mixture shall then be diluted to the mark.

4.2 Yellow mercuric oxide (0.1 g. for each ml. of 0.1*N* acid equivalent to total volatile nitrogen in the mixture) shall be placed in a brown glass bottle of 700-800 ml. capacity. The 500 ml. alkaline mixture shall then be poured in and the stoppered bottle covered with a black cloth. After shaking for one hour and allowing to stand overnight, the stopper shall be removed and replaced, without disturbing the sediment, by a stopper carrying the tubes A, C and E, as shown in Figure F21. A leads to a compressed air outlet, while C is a glass filter tube packed, not too tightly, with clean, dry absorbent cotton.

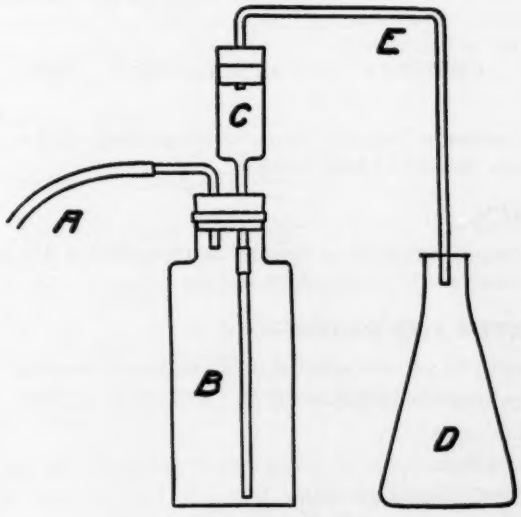

FIGURE F-21

4.3 By applying a moderate air pressure, the supernatant liquid shall be forced through the cotton and collected in a suitable receiver, after discarding the first 20-30 ml. The filtrate shall be tested for ammonia by adding, to a 10 ml. portion, 2 ml. of a solution containing 22.7 g. HgI_2, 33.0 g. KI and 35.0 g. NaOH in 1000 ml. A red color or brown precipitate on heating indicates the presence of ammonia, in which case the determination should be discarded.

4.4 *Total Volatile Amine Nitrogen.* The filtrate from the mercuric oxide precipitate shall be used for total volatile amine nitrogen if no ammonia is present. A 400 ml. portion of the filtrate (par. 4.3) shall be distilled into 25 ml. of 0.1*N* H_2SO_4, and the excess acid titrated with 0.1*N* NaOH. The amount of acid consumed represents four-fifths of the total volatile amine nitrogen of the original sample taken for total volatile nitrogen (Method F20, par. 4.1).

4.5 *Free Ammonia Nitrogen.* The difference between the total volatile nitrogen as determined in Method F20 and the total volatile amine nitrogen, as determined above (par. 4.4) shall be free ammonia nitrogen.

5. RESULTS

5.1 The total volatile amine nitrogen shall be reported in per cent, by volume.

5.2 The free ammonia nitrogen shall be reported in per cent, by volume.

A.L.C.A. Provisional Method February 1954

AMMONIA IN BATE WATERS (F30)

1. SCOPE

1.1 This method is intended for use in determining the free ammonia and total ammonia content of bate liquors.

2. SPECIMEN

2.1 The bate waters shall be sampled as prescribed in Method J30 and a measured volume shall be taken for analysis.

3. APPARATUS AND REAGENTS

3.1 Saturated 95 per cent ethyl alcohol solution of hematine.

3.2 Hydrochloric acid solution: 0.5*N*.

3.3 Kjeldahl unit.

3.4 Kjeldahl flasks.

3.5 Powdered magnesium oxide.

3.6 Methyl orange indicator, 0.1 g. per 100 ml. 95 per cent ethyl alcohol.

4. PROCEDURE

4.1 *Free Ammonia*: *Titration A*. To a 300 ml. sample of bate water shall be added 0.5 to 1.0 ml. saturated alcoholic solution of hematine, and the whole titrated with 0.5*N* HCl to the first color change. In the case of new sulfate bates this color change is to a yellow, and for new chloride bates is to a pink. Old bates may show almost anything from a gray blue to yellow. The end point shall be made to the first permanent color change. (Bate waters from various tanneries exhibit color changes peculiar to each tannery so that it is impossible to define accurately the end point by a description of the color to be expected.)

4.2 *Total Ammonia*: *Titration B*. The titrated solution (par. 4.1) shall be transferred to an 800 ml. Kjeldahl flask and about 1.0 gram of MgO shall be added. The liberated NH_3 shall be distilled into saturated boric acid and titrated with 0.5*N* HCl, using methyl orange as the indicator. Distillation of NH_3 shall be regarded as complete when about 200 to 250 ml. of distillate have passed over.

5. RESULTS

5.1 The free ammonia in the bate water (par. 4.1) shall be reported in per cent, by volume, and calculated as below.

$$\text{Per cent ammonia } (NH_3) = \frac{\text{ml. 0.5 } N \text{ HCl consumed x } 0.85}{300}$$

5.2 The difference between the titration for free ammonia and the titration for total ammonia shall be calculated to ammonium chloride or ammonium sulfate, depending on whichever salt is present in the bate, and the results reported in per cent, by volume.

$$\text{Per cent } NH_4Cl = \frac{(B\text{-}A) \text{ x } 2.675}{300}$$

$$\text{Per cent } (NH_4)_2SO_4 = \frac{(B\text{-}A) \text{ x } 3.3}{300}$$

(Note: As a check on tannery and analytical results, it is helpful to compare the theoretical per cent of ammonium salt with that actually found, especially in the case of freshly made bate waters.)

A.L.C.A. Provisional Method February 1954.

TOTAL CAUSTIC ALKALINITY (F35)

1. SCOPE

1.1 This method is intended to determine the total caustic alkalinity of lime liquors, by titration to pH 10, using the method of Atkin and Atkin.

1.2 According to Atkin and Atkin, at pH 10.0, calcium and sodium hy-

droxide are neutralized practically completely, and ammonium hydroxide is neutralized to the extent of about 24 per cent. The titration will include sodium hydroxide formed by the hydrolysis of sulfides to sulfhydrates, which is practically complete even at the pH value of saturated calcium hydroxide solution but does not include that which would be formed by the further hydrolysis of sulfhydrate to hydrogen sulfide and sodium hydroxide, since this reaction proceeds only to a negligible extent at pH 10.

2. SPECIMEN

2.1 The lime liquor shall be sampled as described in Method J30.

3. APPARATUS AND REAGENTS

3.1 Colorimetric tubes, 50 ml.

3.2 Colorimeter.

3.3 Standard buffer solution of pH 10.0 made by mixing 38 ml. of 0.1*N* ammonium hydroxide and 12 ml. of 0.1*N* ammonium chloride.

3.4 Solution of thymolphthalein (0.2 per cent).

4. PROCEDURE

4.1 A portion of the lime liqour sample shall be filtered through folded filter paper, returning the filtrate until it comes through clear. Into each of two 50 ml. colorimeter tubes shall be pipetted 25 ml. of the filtered liquor, adding to one of the tubes 25 ml. of distilled water. Into a third tube shall be placed 50 ml. of distilled water, and into a fourth tube 50 ml. of a standard buffer solution of pH 10.0. The tube, containing the lime liquor plus water, shall be placed behind the standard buffer in one side of the comparator, and the tube containing water behind the undiluted lime liquor in the other side of the comparator. Ten drops of a 0.2 per cent solution of thymolphthalein shall be added to the standard buffer solution and to the undiluted lime liquor.

4.2 Hydrochloric acid (0.1*N*) shall be added to the undiluted lime liquor, slowly and with stirring, until the color nearly matches that of the standard buffer solution. Then dilute to a volume of nearly 50 ml. with distilled water and continue the titration until an exact color match is obtained.

4.3 A simpler method of determining caustic alkalinity is by calculation from the determination of pH value. The procedure given above is, however, useful in case a potentiometer is not available and also for solutions containing so much sulfide that the electrometric determination of pH value is practically impossible.

5. RESULTS

5.1 The total caustic alkalinity shall be calculated according to the

following formula and the results reported in terms of normality.

$$\text{Total Caustic Alkalinity in Normality} = \frac{A-0.24B}{250}$$

where A is the number of ml. 0.1*N* HCl required to titrate 25 ml. of lime liquor to pH 10 (par 4.2) and B is the number of ml. of 0.1*N* acid required for the total volatile nitrogen of 25 ml. of lime liquor (Method F20, par. 4.).

A.L.C.A. Provisional Method February 1954.

CALCIUM IN BEAMHOUSE LIQUORS (F40)

1. SCOPE

1.1 This method is intended for use in determining the lime content of lime liquors and the calcium content of soak and bate waters.

2. SPECIMEN

2.1 The beamhouse liquor shall be sampled as described in Method J30. For the analysis of lime liquors 50 ml. of sample shall be employed and for analysis of soak or bate waters 200 ml. shall be used.

3. APPARATUS AND REAGENTS

3.1 Drying chamber.

3.2 Tared platinum crucible.

3.3 Saturated solution of ammoinum oxalate.

3.4 Potassium permanganate (0.1*N* solution).

4. PROCEDURE

4.1 To a beaker, containing the beamhouse liquor (50 ml. for lime liquors and 200 ml. for soak and bate waters) shall be added enough hydrochloric acid to make the solution slightly acid. After filtering through a folded filter paper and returning the filtrate until it comes through clear, the filter paper shall be washed with distilled water until free from chlorides, adding the wash water to the filtrate.

4.2 The filtrate shall be made slightly alkaline with ammonia, heated to boiling and shall have added to it 35 ml. of a saturated solution of ammonium oxalate. Boiling shall be continued until the precipitated calcium oxalate becomes granular. After standing until the precipitate has settled, the solution shall be filtered through fine filter paper and washed thoroughly with dilute (2 per cent) ammonium hydroxide. The precipitate shall be redissolved in a little dilute hydrochloric acid, receiving the solution in a beaker in which the original precipitation was made and washing the paper thoroughly with hot water. After reprecipitating with ammonia and ammonium oxalate, as described above, the precipitate shall be filtered off and wash-

ed free from chlorides. The determination may be completed by either of the following modifications.

4.3 *Gravimetric procedure.* The precipitate and filter paper shall be ignited in a covered platinum crucible, then cooled in a desiccator and weighed rapidly. Ignition shall be repeated until constant weight is obtained.

4.4 *Volumetric procedure.* The point of the filter paper shall be broken with a platinum wire and the precipitate washed into the beaker in which the calcium was precipitated, using hot H_2SO_4 (1 to 1) and hot water. The paper in the funnel shall be washed with successive portions of hot acid and hot water until all the precipitate has been washed or dissolved from the paper. The contents of the beaker shall be heated to about 90° C. making sure that all the precipitate is dissolved, and shall be titrated while hot with 0.1*N* $KMnO_4$ until one drop produces a permanent pink. Finally the filter paper shall be added to the beaker and the titration completed, if additional $KMnO_4$ is necessary.

5. RESULTS

5.1 The percentage of calcium oxide in the beamhouse liquor or the pounds of commercial lime per gallon shall be reported.

5.2 The calculation of grams CaO per 100 ml. of liquor shall be made as follows:

Gravimetric—CaO(g. per 100 ml.) =Weight CaO x 2

Volumetric—CaO(g. per 100 ml.) =ml. 0.1*N* $KMnO_4$ x factor x 0.005608

5.3 The results in par. 5.2 may be calculated to pounds per gallons, in terms desired, by the following.

Lbs. CaO per gal. =Grams CaO per 100 ml. x 0.08346

Lbs. $Ca(OH)_2$ per gal. =Grams CaO per 100 ml. x 0.11028

$$\text{Lbs. commercial lime per gal.} = \frac{\text{Lbs. CaO [or } Ca(OH)_2\text{] per gal. x 100}}{\%\text{ available CaO (or } Ca(OH)_2\text{) in lime}}$$

A.L.C.A. Provisional Method February 1954.

CHLORIDES IN BEAMHOUSE LIQUORS (F50)

1. SCOPE

1.1 This method is intended for use in determining the chloride content of lime liquors as well as of soak and bate waters.

2. SPECIMEN

2.1 The liquor shall be sampled in accordance with the instructions of Method J30 and a 20 ml. portion of the filtered liquor shall be taken for analysis.

3. REAGENTS

3.1 Standardized 0.1*N* silver nitrate.

3.2 Nitric acid, concentrated.

3.3 Ferric alum indicator solution, 10 g. pure ferric alum dissolved in 100 ml. of hot 7.5 per cent nitric acid.

3.4 Standardized 0.1*N* potassium thiocyanate.

4. PROCEDURE

4.1 A 20 ml. portion of the filtered liquor shall be pipetted into a 100 ml. volumetric flask and diluted to the mark with distilled water. To a 15 ml. aliquot of the thoroughly shaken mixtures, pipetted into an Erlenmeyer flask, shall be added 25 ml. of 0.1*N* $AgNO_3$, followed by 10 ml. of concentrated HNO_3.

4.2 The above dilution and quantity of $AgNO_3$ is based on the assumption that not more than 4 g. of NaCl is present in 100 ml. of liquor. If less than 0.5g. of NaCl is present in 100 ml. of liquor, the dilution of liquor shall be omitted, and a 15 ml. aliquot of the original sample analyzed directly.

4.3 The mixture shall be heated to just below boiling and maintained at that temperature for from 2 to 3 hours. The solution shall be cooled, diluted to about 100 ml. with distilled water, 5 ml. of ferric alum indicator added and the excess $AgNO_3$ shall be determined by titration with 0.1*N* KSCN. The end point is indicated by the formation of the brownish red $Fe(SCN)_3$, which may be readily observed if the precipitate of AgCl and AgSCN is allowed to settle.

5. RESULTS

5.1 The soluble chloride content of the liquor shall be reported as per cent sodium chloride, by volume.

A.L.C.A. Provisional Method February 1954.

SULFIDES IN LIME LIQUORS (F51)

1. SCOPE

1.1 This method is intended for use in determining sulfides in beamhouse liquors.

2. SPECIMEN

2.1 The liquor shall be sampled as described in Method J30 and 25 ml. of filtered liquor shall be taken for analysis.

3. APPARATUS AND REAGENTS

3.1 Spot plate.

3.2 0.1*N* zinc sulfate solution (28.75 g. $ZnSO_4.7\ H_2O$, 50 g. ammonium chloride and 50 ml. of concentrated ammonium hydroxide per liter, standardized against standard potassium ferrocyanide solution).

3.3 Freshly prepared solution of sodium nitroprusside solution (0.1 g. per 100 ml.).

4. PROCEDURE

4.1 A 25 ml. portion of filtered liquor shall be pipetted into a beaker and titrated with 0.1*M* zinc sulfate solution. A freshly prepared sodium nitroprusside solution shall be used as an external indicator on a spot plate. The zinc sulfate solution is added until a drop of the mixture transferred to a drop of the indicator on the spot plate produces only a faint blue color, which does not change with further addition of zinc sulfate.

4.2 If the volume of zinc sulfate solution consumed is less than 6.5 ml., the figure shall be used for the calculation of the sulfide content. If the volume exceeds 6.5 ml., the titration shall be repeated as follows. A second 25 ml. portion of liquor shall be pipetted into a 250 ml. volumetric flask to which shall be added an accurately measured volume of 0.1*M* zinc sulfate, slightly less in amount than that required in the first titration, and the whole made to volume with distilled water. The contents of the flask shall be filtered through a dry filter paper, discarding the first 25 ml. of filtrate. A 50 ml. aliquot of the filtrate shall be pipetted into a beaker and the 0.1*M* zinc sulfate added drop by drop, spotting as before after each addition, until the blue color is no longer produced.

5. RESULTS

5.1 The sulfide in the liquor shall be reported as per cent, by volume, or as pounds of sulfide per gallon.

5.2 Where the original titration exceeded 6.5 ml. of zinc sulfate, the second determination shall be recorded as A = ml. 0.1*M* zinc sulfate added before filtering and B = ml. added to the aliquot after filtration. Accordingly,

Grams Na_2S per 25 ml. lime liquor = (A + 5B) x 0.0078
Grams BaS per 25 ml. lime liquor = (A + 5B) x 0.0169

5.3 The results shall be calculated to pounds of sulfide per gallon, in terms of whatever sulfide is used in the process, by the following expressions.

Lbs. Na_2S (100%) per gal. = (A + 5B) x 0.00260
Lbs. Na_2S (60%) per gal. = (A + 5B) x 0.00434
Lbs. BaS (100%) per gal. = (A + 5B) x 0.00564
Lbs. BaS (60%) per gal. = (A + 5B) x 0.00868

A.L.C.A. Provisional Method February 1954.

SULFATES IN BEAMHOUSE LIQUORS (F52)

1. SCOPE

1.1 This method is intended for use in determining the sulfate content of beamhouse liquors, particularly bate waters.

2. SPECIMEN

2.1 The beamhouse liquor shall be sampled in accordance with Method J30 and 50 ml. of filtered liquor shall be taken for analysis.

3. APPARATUS AND REAGENTS

3.1 Dry chamber.

3.2 Tared crucible.

3.3 Sodium peroxide.

3.4 Ten (10) per cent solution of barium chloride.

4. PROCEDURE

4.1 Fifty (50) ml. of the filtered liquor shall be pipetted into a beaker and diluted to about 200 ml. About 1 g. of sodium peroxide shall be added, in small increments, to destroy organic matter. After boiling for about 20 minutes, the solution shall be neutralized with HCl, adding 1.0 ml. excess, and then about 10 ml. of a 10 per cent barium chloride solution shall be added drop by drop with stirring. After settling over night, the precipitate shall be filtered off using a Whatman No. 44 paper, or its equivalent, and washed free from chlorides. The precipitate shall be ignited in a weighed crucible, beginning at a low temperature and ending at the highest temperature attainable with an ordinary Bunsen burner, allowing free access of air to the contents of the crucible. The ash shall be cooled in a desiccator and weighed.

5. RESULTS

5.1 The sulfates shall be reported as sulfur trioxide in per cent, by volume.

$$\text{Per cent } SO_3 = \frac{\text{g. } BaSO_4 \times 0.343}{\text{ml. liquor taken}}$$

A.L.C.A. Provisional Method February 1954.

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pH VALUES OF BEAMHOUSE LIQUORS (F60)

1. SCOPE

1.1 This method is intended to determine the pH values of the various liquors (soak waters, lime liquors, warm water pools, bate waters) employed in the beamhouse.

2. SPECIMEN

2.1 The liquors shall be sampled as described in Method J30 and the liquors employed for pH determination, shall be unfiltered.

3. APPARATUS

3.1 pH meter (potentiometer) equipped with glass electrodes. Where liquors of pH value higher than 9.0 are being tested (e. g. lime liquors) the pH meter shall be equipped with special electrodes for alkaline solutions [E. R. Theis and M. O. Ricker, *J. Am. Leather Chemists Assoc.*, **35**, 663 (1940)].

3.2 Standard buffer solutions of pH 4.01, 7.0, and 9.18 [E. R. Smith and R. G. Bates, *J. Soc. Leather Trades Chemists*, **34**, 397 (1950), and pH 10 and 12.5 (Lloyd E. West, *Anal. Chem.* **23**, 1562 (1951); W. M. Tuddenham and D. H. Anderson, *ibid.* **22**, 1146 (1950)].

4. PROCEDURE

4.1 Prior to the test the pH meter shall be standardized with a standard buffer of pH as close as possible to the expected pH value. The pH meter shall be standardized periodically against two or more standard buffers covering the working pH range.

4.2 The pH value shall be determined on the unfiltered beamhouse liquor at 25° ± 5° C. Where alkaline liquors, such as lime liquors, are being tested, the pH meter shall be equipped with alkaline type electrodes.

5. RESULTS

5.1 The pH values shall be reported to the nearest 0.1 pH unit.

A.L.C.A. Provisional Method February 1954.

TOTAL SOLIDS AND ASH IN LEATHER FINISH (K1)

1. SCOPE

1.1 This method is intended for use in determining the total solids content and the ash content of a finishing material before its use on any leather.

2. SAMPLE

2.1 One 5 gram and one 10 gram sample of finishing material shall be weighed with accuracy to within 0.001 gram.

3. APPARATUS

3.1 Two platinum dishes tared.

3.2 Drying oven that operates at 110° F. ± 5° F. and 200° F. ± 5° F.

3.3 Desiccator with calcium chloride or other desiccant.

3.4 Muffle furnace capable of maintaining temperature of 600° C. ± 25° C.

4. PROCEDURE

4.1 *Total Solids.* Samples, weighed in platinum dishes, shall be placed in oven for 16 hours at 110° F. followed by 2 hours at 200° F. (If two ovens at different temperatures are not available, the oven temperature in the first oven should be increased for the 2 hour heating). The dishes shall be removed from the oven, placed in a desiccator for one hour to cool to room temperature and weighed. The dishes shall be returned to the oven for one hour at 200° F. and, after cooling in a desiccator for one hour, shall again be weighed. If the loss in the one hour drying period did not change the total solids percentage more than 0.1%, the results shall be reported. If greater than 0.1% loss in weight was obtained from the last one hour drying period, then the drying shall be repeated until the change is less than 0.1%.

4.2 *Ash.* The platinum dish, containing the residue from the total solids determination, shall be placed in a muffle furnace at 600° C. ± 25° C. for 2 hours. If difficulty is encountered in completely burning off the carbon, the residue shall be leached with hot water (filtering through ashless filter paper) and residue further ignited in the muffle furnace. To the dish containing the cooled ash, the filtrate shall be added, evaporated to dryness and heated for 30 minutes at 600° C. The product shall then be cooled in a desiccator and weighed.

5. RESULTS

5.1 The total solids of the finishing material shall be reported in per cent.

5.2 The ash content of the finishing material shall be reported in per cent.

A.L.C.A. Provisional Method February 1954.

NITROCELLULOSE IN FINISH ON LEATHER (K5)

1. SCOPE

1.1 This method is intended for use in determining nitrocellulose in finish on all types of leathers.

2. SPECIMEN

2.1 The specimen shall be approximately 1 cm. square of finished leather.

3. APPARATUS AND REAGENTS

3.1 Pyrex watch glass, 100 mm. diameter.

3.2 Two reagent bottles (4 fl. oz. each) equipped with glass joint dropping pipette.

3.3 Indicator solution prepared by dissolving 0.1 g. of diphenylamine in solution containing 100 ml. of sulfuric acid and 30 ml. of distilled water.

3.4 Blank solution comprising 100 ml. of sulfuric acid and 30 ml. of distilled water.

3.5 Acetone, C. P.

4. PROCEDURE

4.1 The specimen shall be placed in the watch glass with the finish side up. One or 2 ml. of indicator solution shall be applied on the finish and allowed to run over the side of the leather onto the watch glass. After three minutes, if the indicator solution does not develop a dark blue color, then nitrocellulose lacquer is not present in finish. If indicator solution develops a dark blue color after contact with finish, it indicates presence of nitrocellulose lacquer or has developed color from colored finishing materials or both.

4.2 The above procedure shall be repeated except that the blank solution is employed instead of the indicator solution. If a dark blue color does not develop, whereas it does with the indicator solution, then nitrocellulose is present in the finish and colored finishing materials do not interfere.

4.3 If colored finish material develops a dark blue color in presence of the blank solution, then the specimen shall be placed in a watch glass with the finish side up and acetone shall be poured on the specimen, until completely covered, for dissolving any nitrocellulose present in the specimen. After allowing the specimen to soak in acetone for approximately two minutes, the specimen shall be removed from the watch glass and the acetone in the watch glass evaporated on the steam oven to dryness. When cooled to room temperature, a few drops of indicator solution shall be dropped on one side of the watch glass near the rim and the drops allowed to run downward. At another location on the watch glass, a few drops of blank solution shall be placed near the rim and allowed to run downward. If lacquer is present in the finish, a dark blue color will develop as the indicator solution runs downward in the watch glass and the blank solution will not show any color development.

5. RESULTS

5.1 The indicator method for testing the presence of nitrocellulose in finish on leather shall be reported as positive or negative.

A.L.C.A. Provisional Method February 1954.

FLEXIBILITY AND ADHESION OF FINISH ON LEATHER (K10)

1. SCOPE

1.1 This method is intended for use on finished upper leather, for shoes or similar end use, or the leather article, such as shoe, hand bag, to measure flexibility and adhesion of finish on leather.

2. APPARATUS AND REAGENTS

2.1 Air tight oven at 110° F. ± 5° F.

2.2 Calcium chloride as desiccant spread thinly in tray near bottom of oven with surface area at least 50% of surface area of bottom of oven.

2.3 Desiccator at room temperature with calcium chloride as desiccant.

3. PROCEDURE

3.1 The sample shall be placed in the oven at 110° F. ± 5° F. for 24 hours, after which time the sample is removed from the oven and placed in a desiccator at room temperature for 2 hours. After removing from the desiccator, the sample shall be bent sharply at 180° angle by hand with the finish side on the inside of bend, pressing tightly together with fingers and rolling back and forth for three complete cycles a distance of approximately 0.25 inch. Examination of finish crack shall then be made.

4. RESULTS

4.1 Flexibility shall be visually observed and reported as one of following: No cracking, slight cracking or considerable cracking.

4.2 Adhesion shall be visually observed for looseness of finish that can be wiped off with fingers and reported as one of following: good, fair or poor.

A.L.C.A. Provisional Method February 1954.

TACKINESS OF FINISH ON LEATHER (K11)

1. SCOPE

1.1 This method is intended for use on finished upper leather, for shoes or similar end use, or the leather article, such as shoe, hand bag, to measure both dry, warm and moist, warm tackiness.

2. APPARATUS AND REAGENTS

2.1 Air tight oven at 110° F. ± 5° F.

2.2 Calcium chloride as desiccant spread thinly in tray near bottom of oven with surface area at least 50% of surface area of bottom of oven.

2.3 Humidifier cabinet at 90% relative humidity ± 5% and 90° F. ± 2° F.

3. PROCEDURE

3.1 The sample shall be placed in oven at 110° F. ± 5° F. for two hours after which time the sample shall be removed from oven and immediately felt with clean dry fingers for tackiness.

3.2 Another similar sample shall be placed in humidifier at 90% relative

humidity and 90° F. ± 2° F. for 24 hours. After removing from humidifier, the sample shall be felt immediately with clean dry fingers for tackiness.

4. RESULTS

4.1 Dry, warm tackiness of finish shall be reported as one of following: no tackiness, slight tackiness or considerable tackiness.

4.2 Moist, warm tackiness of finish shall be reported as one of following: no tackiness, slight tackiness or considerable tackiness.

A.L.C.A. Provisional Method February 1954.

The Effect of Splitting on the Tensile Properties of Leather*

By MIETH MAESER and O. J. DION

Several kinds of leather are used in making holddown covers, pad covers, toe formers, heel straps, and other parts used on shoe machinery. In order to select the type of leather, which of the three splits (flesh, corium, or grain), and the thickness to use for a particular part, a rather complete knowledge of the properties of each leather is required.

Several leathers have been tested. The results which were obtained on heavy chrome tanned leather, and the methods used to interpret them are presented in this paper.

TESTS ON CHROME TANNED SPLITS

Test Specimens

Two heavy chrome tanned skins in the blue, lightly fat-liquored, and with a minimum thickness of 220 mils were cut into 800 pieces 1½" x 6", with the long axes normal to the backbone. The pieces were piled on the floor, mixed thoroughly, and separated at random into 24 groups of 33 pieces. Ten of the groups were used in burst tests. The remaining fourteen groups were prepared for tensile tests as shown in Table I.

A. One group of 33 pieces was kept unsplit.

B. The specimens of a second group were split individually a few mils at a time until the flesh layer of each piece was just removed.

C. The remaining 12 groups were split to an average thickness of 209 mils, which entirely removed the flesh layer from all the specimens. Eleven of these twelve groups were split into a corium split and a grain split.

*Presented at the Golden Jubilee Meeting of the A.L.C.A. in Cincinnati, Ohio, June 8, 1953.

After splitting, some of the groups were so near alike in strength and thickness, that the data overlapped. Such groups were averaged together and handled as a single group.

TABLE I

GROUP	NUMBER OF SPEC.	AVERAGE THICKNESS MILS	
		CORIUM SPLIT	GRAIN SPLIT
1	33		251
2	33		220
3	33		209 — Averaged
4	33	Fell Apart	200 — Averaged
5	33	30	179
6	33	40	167 — Averaged
7	33	55	154
8	33	82	128
9	33	110	100
10	33	133	76
11	33	154	57
12	33	165 — Averaged	45
13	33	172 — Averaged	37 — Averaged
14	33	186	26 — Averaged

Test Method

Tensile specimens were cut, measured, and tested in accordance with the A.L.C.A. Method for Tensile Strength.

Results

A. Breaking Load of Corium Splits

The load at which each specimen broke was observed and divided by the width to obtain the breaking load in pounds per inch of width. This value was plotted against the thickness of the specimen in the scatter diagram of Figure 1. The average thickness was plotted against the average breaking

load for each group, and a solid line was drawn through the points to show the central tendency of the data.

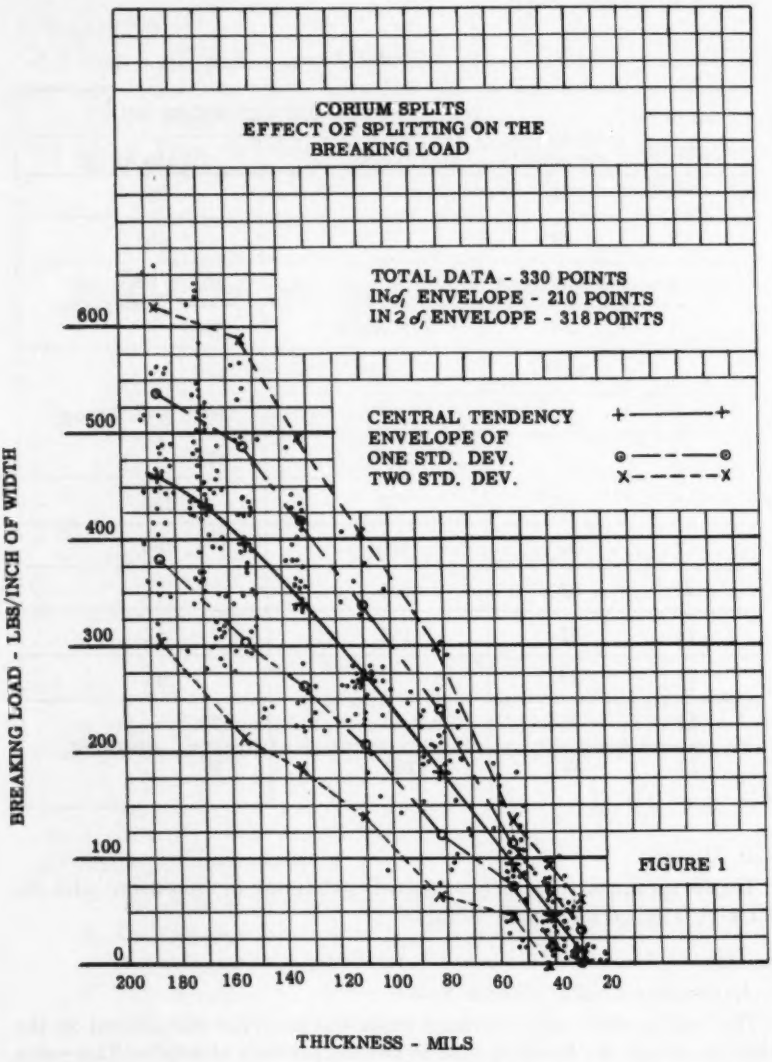


FIGURE 1

Several facts regarding the relation between the breaking load and the thickness are shown by this plot.

1. The average breaking load does not vary as a straight line with the thickness, but curves slightly. In the thickness range of 30 to 120 mils, which is the range in which most leather is cut, the average line is so nearly straight that using it as such would introduce no appreciable error.
2. The central tendency curve does not pass through the origin, but interests the thickness axis at approximately 30 mils; indicating that corium splits thinner than 20 to 30 mils have little or no strength.
3. There is a wide variation in the breaking load at each thickness; and it is impossible to predict a single value of the breaking load from a single value of the thickness. No single value formula can be written as suggested by Kanagy [1], nor can any single line be drawn as suggested by Wilson and Kern [2], that will fully express the relationship which exists between the two variables.

If the full meaning of such data is to be expressed, some means must be used to indicate the magnitude of the variation in the breaking load, and the manner in which the individual values are distributed about the average value. The standard deviation is such a value. It is the best single means which has been devised to evaluate the variation which exists in a group of data with normal distribution.

The standard deviation of the breaking load was calculated for each group and plotted on Figure 1 as circled dots above and below the average. A dot-dash line was drawn between these points. Two standard deviations were plotted as crosses above and below the average and a dotted line was drawn between the points.

Eliminating the data for the group with an average thickness of 30 mils because the strength of many of the specimens in the group was zero, there remained a total of 293 points on the plot. In the envelope of one standard deviation there are 200 points, or between 67 and 68 per cent of the data. In the envelope for two standard deviations, there are 207 points, or approximately 94 per cent of the data, showing that the test data on which complete results could be obtained very closely follows a normal, unbiased distribution.

The standard deviations of the breaking load are tabulated in Table II, Column 3, as pounds per inch of width. As the thickness decreases, the magnitude of the deviation, expressed in absolute units decreases. If, however, the standard deviation in the breaking load is expressed as a per cent of the average, the values in the last column of Table II are obtained. These are the coefficients of variation.

There is a small increase in the coefficients of variation as the thickness is reduced from 186 to 110 mils, and then a sharp increase as the splits become still thinner. It seems likely that this increase is due to the fact that the strength of coarse fibered leather is affected more by splitting than that of

TABLE II

THICKNESS MILS	AVERAGE BREAKING LOAD LBS./IN. WIDTH	STANDARD DEVIATION	
		LBS./IN. WIDTH	% AVERAGE
30	10	7.5	75
40	44	26	59
55	94	42	45
82	181	59	32
110	272	67	25
133	339	78	23
154	395	92	23
165 172 Ave.	430	95	22
186	460	97	21

fine fibered leather, and as the specimens become thinner, this difference in the splitting effect becomes an increasingly greater percentage of the breaking load, resulting in larger coefficients of variation.

In order to make the curves easier to read, the central tendency curve of Figure 1 and the coefficients of variation of Table II were plotted in Figure 2. These curves completely interpret the relation between the breaking load and thickness, and can be used to select a leather thickness which will have any desired probability of giving a specified minimum breaking load.

Consider the problem of specifying the thickness of a leather part which requires a breaking load of approximately 250 lbs./in. of width. If a thickness of 100 to 110 mils, which gives an average breaking load of 250 lbs./in. of width, was selected for the part, one-half of all the pieces would be weaker than desired. This condition would result in a large number of early failures and would almost certainly not be tolerated.

If a thickness of 120 to 130 mils was selected, an average breaking strength of 300 to 330 lbs./in. of width and a coefficient of variation of 23 to 24 per cent, or ± 72 lbs./in. of width, would be obtained. With this thickness,

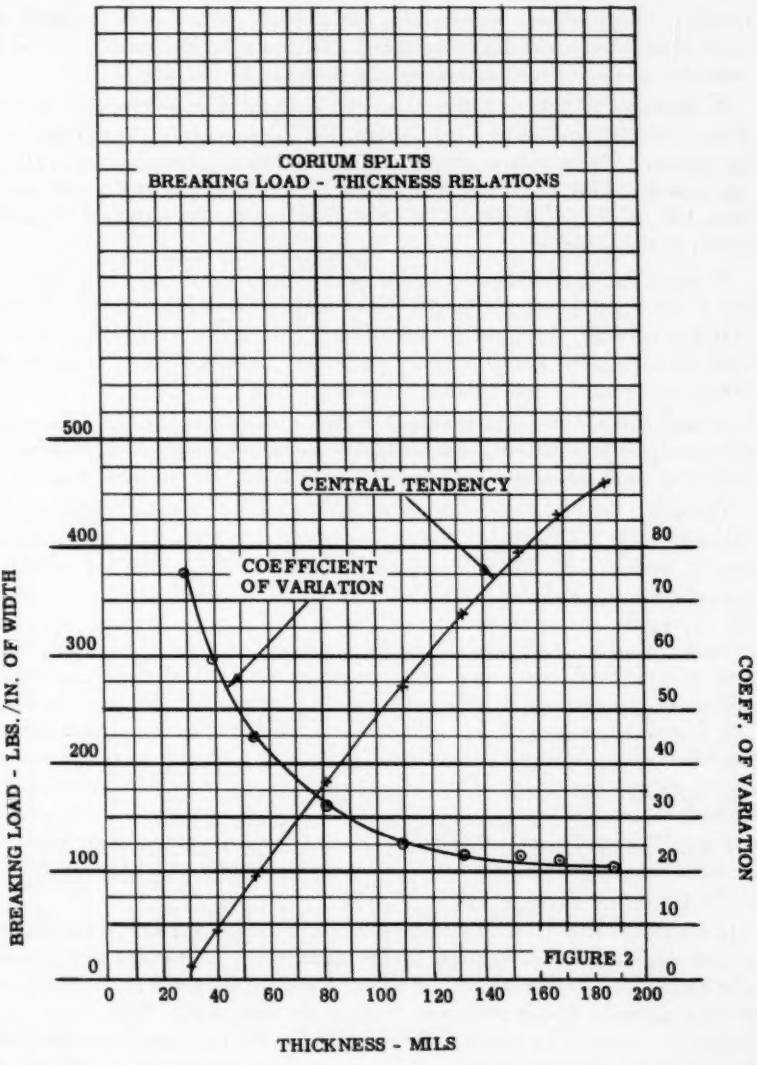


FIGURE 2

84 per cent of the pieces would have a breaking load of 240 lbs./in. of width or greater, and the breaking load of 97 per cent of the parts would be above 171 lbs./in. of width. If the part was to be used by the maker of the part, this would probably be very close to the optimum thickness. Some parts

would fail far too soon, but the loss due to early failure would probably be more than offset in cutting economies. If, however, the parts were to be sold, the number of early failures would probably be too high.

A thickness of 130 to 140 mils would give an average breaking load of 330 to 360 lbs./in. of width, with a coefficient of variation of 22 to 23 per cent. By the laws of probability, over 84 per cent of the parts would have a breaking load of 270 lbs./in. of width or greater, and 97 per cent would be stronger than 195 lbs./in. of width. This should be satisfactory strength for even a high quality product.

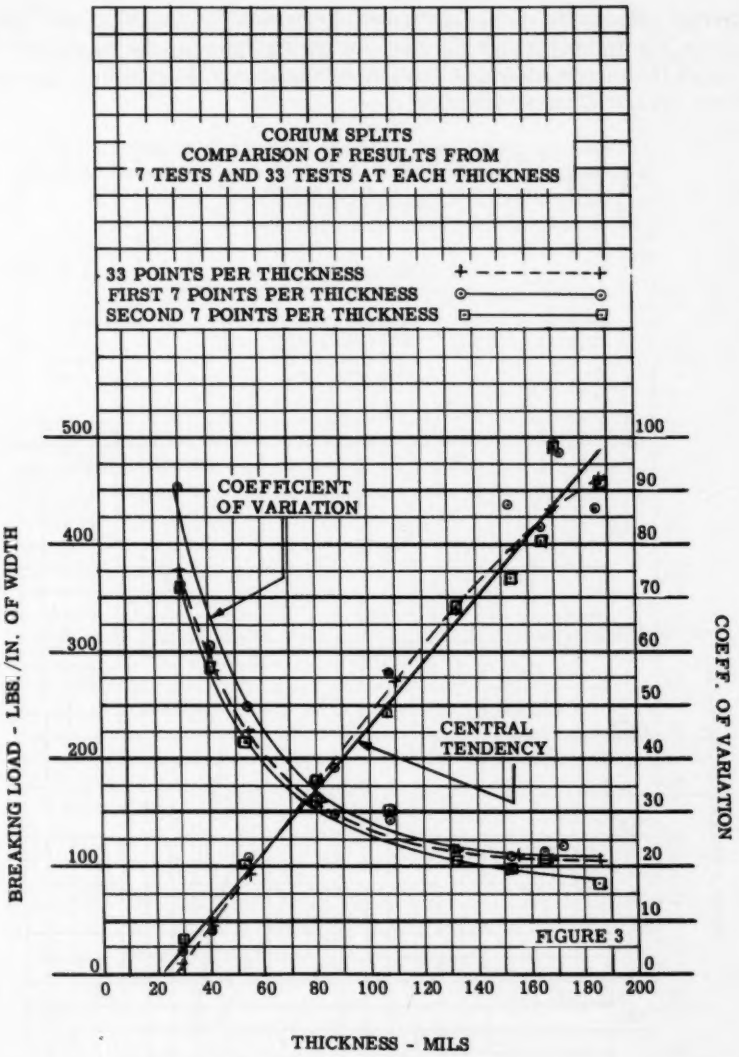
It is evident that if the service life of this part is determined by strength alone, some parts will last nearly twice as long as others. There is little that can be done about such a condition. The fact of variation in service must be recognized and accepted. Variability never can be eliminated entirely, nor reduced economically to too low a level.

A large number of tests were made in this work so that the complete range of variations which exist in leather would be determined beyond any reasonable doubt. It can be demonstrated that fewer tests will give the same results.

The first five tests from each group were averaged and the coefficients of variation were determined. The results were plotted and the best possible smooth curve drawn through each set of points. The curves for both the central tendency and the coefficient of variation departed significantly from the curves for the large sample, indicating that 5 tests at each thickness formed a sample which was too small to properly interpret the data. The first six tests from each group were treated in the same way, but again the curves were significantly different from the curves for the large sample. The first seven tests made at each thickness were then averaged and the coefficients of variation were determined. Both sets of data were plotted as circled dots in Figure 3, and the curves most closely representing the points for both central tendency and coefficient of variation were drawn. The curves of Figure 2 were drawn on Figure 3 as dotted lines for comparison. There is no significant difference between the two sets of curves at any point except in the coefficient of variation at 30 mils.

It is possible that the curve through the averages of the first seven points at each thickness agreed with the curves through the average of the 33 points only by chance. This was checked by using the second seven tests from each group separately, but in the same way as the first seven. The results are plotted on Figure 3 as squares. The curves for the two small samples, and the curves for the large sample all agree closely except in the coefficient of variation at 30 mils.

The probabilities that two successive samples would agree by chance so closely with each other, and with a third much larger sample are very small. It must be concluded that seven random specimens at each of several thick-



nesses are sufficient to establish both the central tendency and the coefficient of variation with the required accuracy.

It should not be concluded from the above demonstration that seven specimens tested at one thickness are enough to give either a dependable

average value or the correct coefficient of variation for that thickness. When curves are drawn through the data for several groups, the interpretation at each thickness is influenced by all the other data so that in each of the above cases, 63, not 7, tests were used.

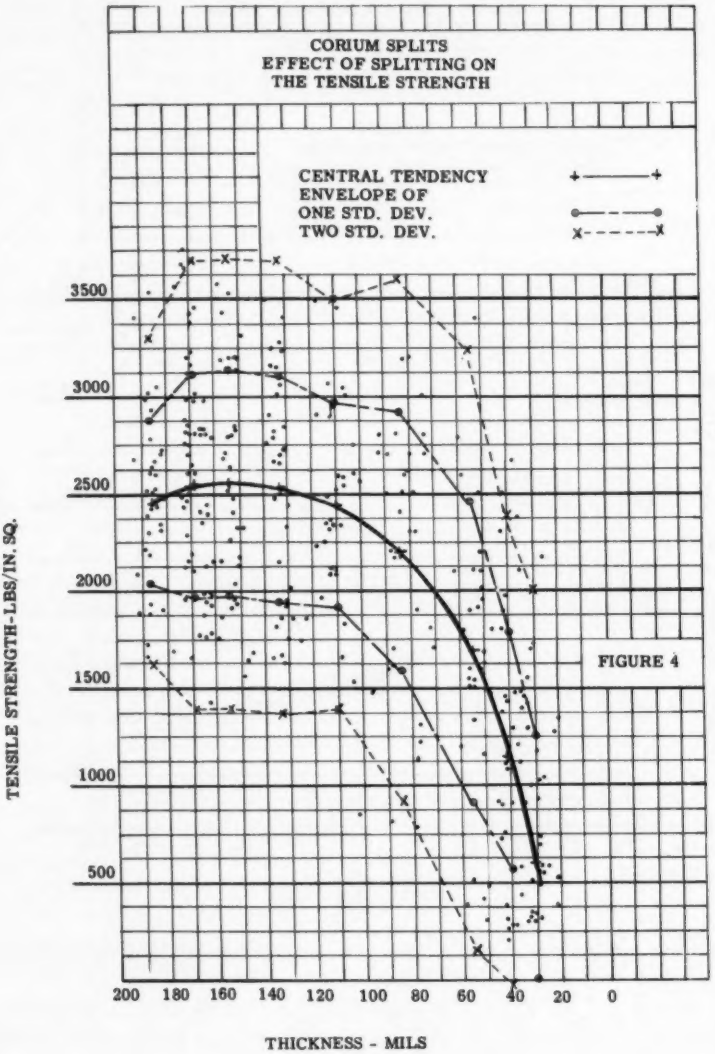


FIGURE 4

B. Tensile Strength of Corium Splits

The tensile strength of each corium specimen was determined and plotted against its thickness to give the scatter diagram of Figure 4. The central

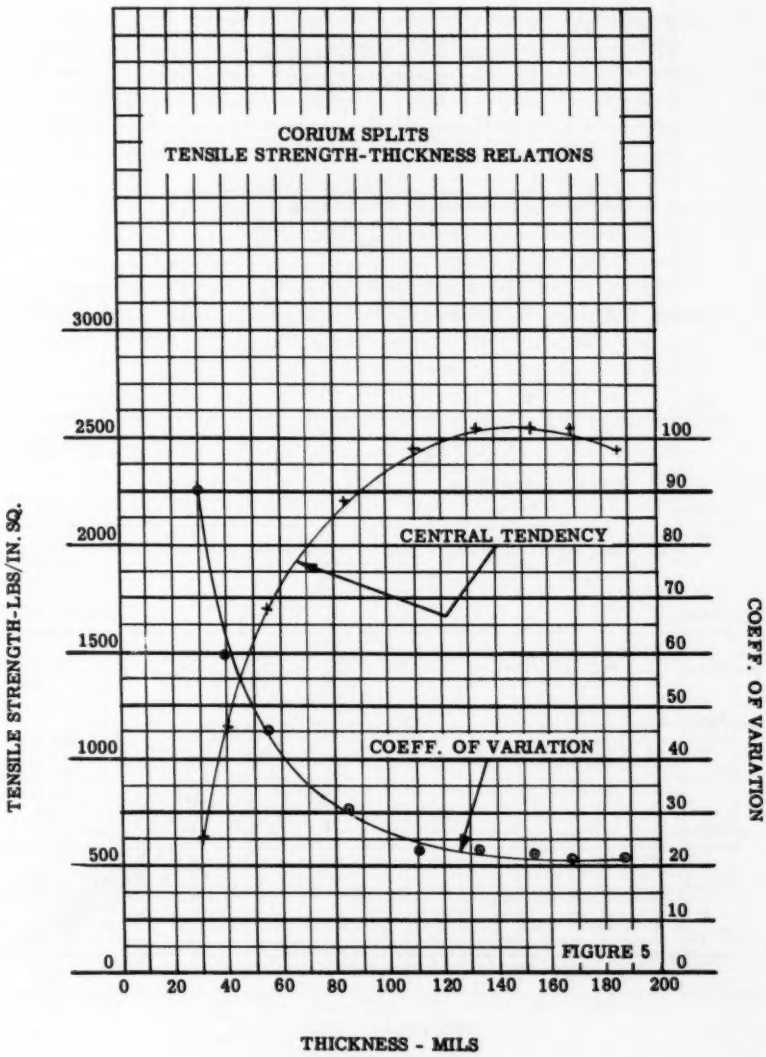


FIGURE 5

tendency curve and the one and two standard deviation envelopes are shown. The central tendency curve of Figure 4 and the coefficients of variation for the tensile strength were plotted in Figure 5.

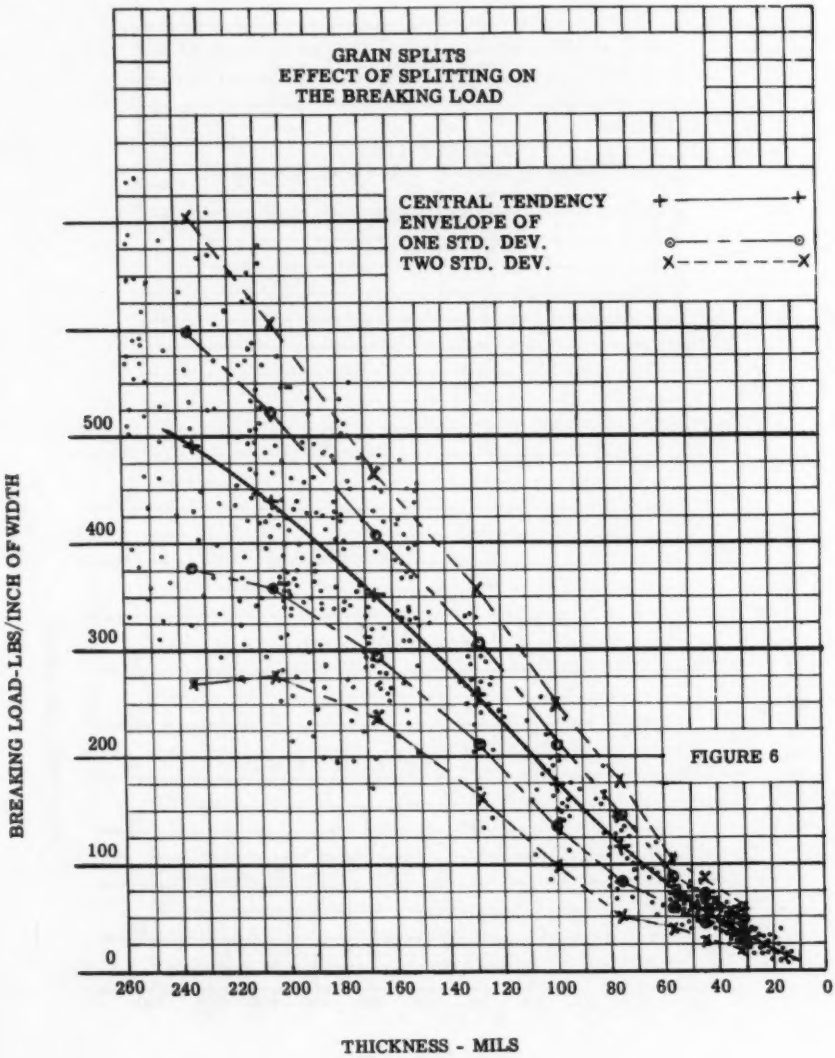


FIGURE 6

The plots show that splitting has practically no effect on the tensile strength until the thickness is reduced below 120 mils. The strength then drops rapidly and becomes zero for splits varying in thickness from 20 to 30 mils. As would be expected, the coefficients of variation for the tensile strength

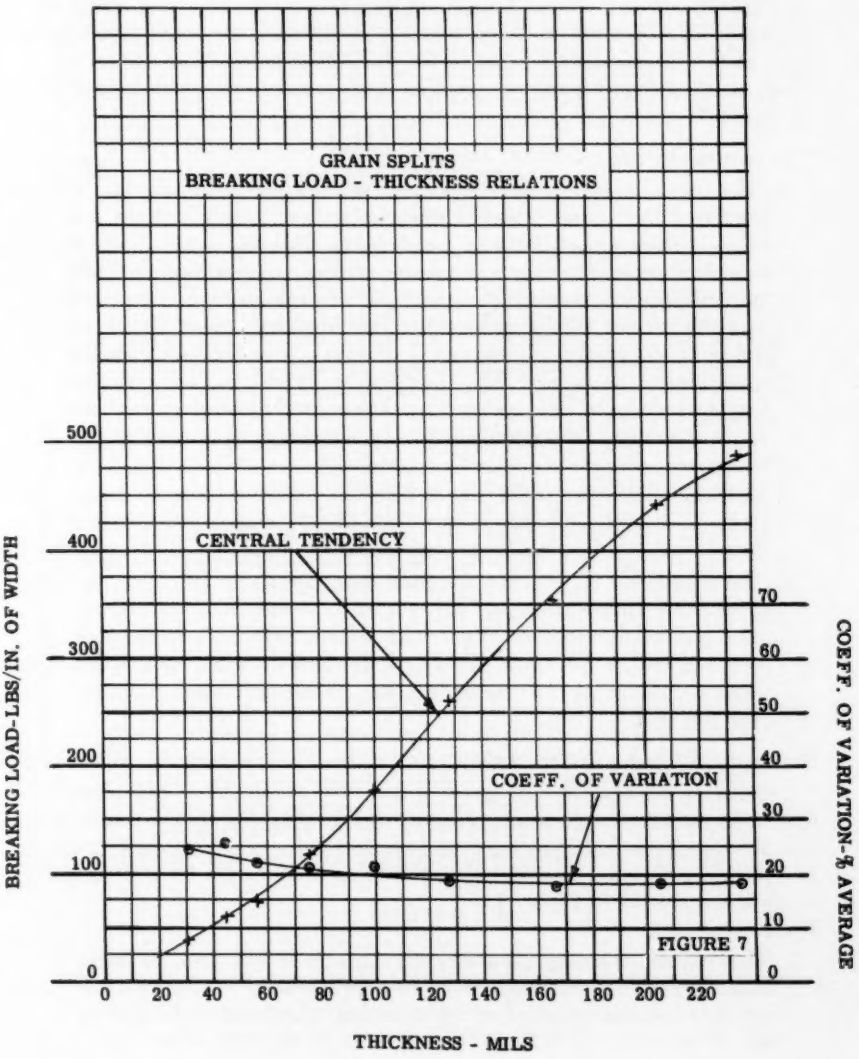


FIGURE 7

are very nearly equal to those for the breaking load; varying from approximately 20 per cent for the thick, to 75 per cent for the thin specimens.

C. Breaking Load of Grain Splits.

The breaking load for each specimen cut from the grain splits of Table I, was determined and plotted against its thickness in the scatter diagram of Figure 6. The central tendency curves and standard deviation envelopes were plotted in the same manner as for the corium splits. The central tendency curve of Figure 6 and the coefficients of variations are plotted together in Figure 7.

The plot shows that:

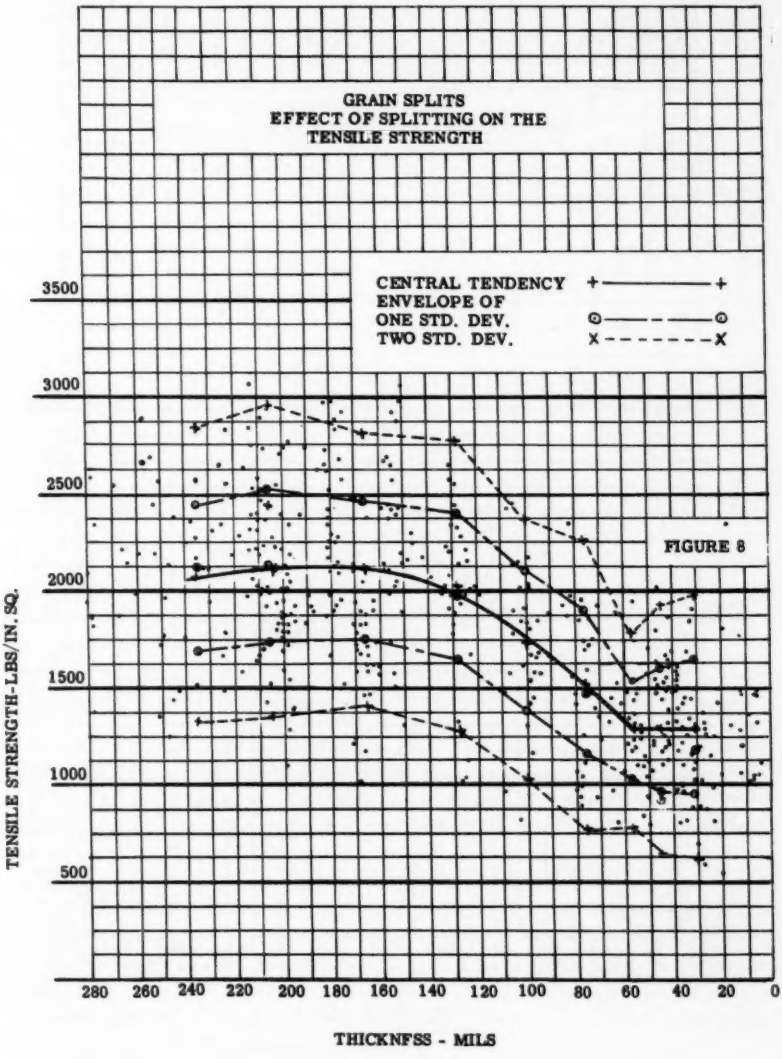
1. The central tendency curve for grain splits is not a straight line as suggested by Kanagy [1], and it departs farthest from a straight line below a thickness of 100 mils, which is the thickness range in which most leather is split. There is a section of the curve between 100 and 160 mils which is essentially straight. If this section were interpreted as a straight line and extrapolated to zero breaking load, it would cut the thickness axis at approximately 35 mils. Such an interpretation would agree closely with Kanagy's results. However, the breaking load does not go to zero at some finite thickness, but bends toward the origin of the plot, and grain splits as thin as 5 mils have measureable strength.
2. Corium splits with a thickness of 40 mils or more are stronger than grain splits of equal thickness, but when the splits are reduced to less than 40 mils, the grain splits are the stronger.
3. The coefficients of variation for grain splits are less than for corium splits, being approximately 18 per cent as compared to 21 per cent for thick specimens, and only 21 per cent as compared to 70–75 per cent for specimens 30 mils thick. This indicates that the grain layer is less sensitive to splitting than the corium, and its strength is more uniform over the skin.

D. Tensile Strength of Grain Splits.

The tensile strength of each grain specimen was calculated and plotted against its thickness in the scatter diagram of Figure 8. The central tendency curves and standard deviation envelopes are shown as in previous cases. The central tendency curve and the coefficients of variation for the tensile strength are plotted in Figure 9..

These plots show:

1. That the tensile strength is practically constant at 2000 p.s.i. for thicknesses above 120 mils; then drops to approximately 1250 p.s.i. at 60 mils and remains constant as the thickness is reduced to 10 mils or less.



2. That the tensile strength of thick grain specimens is less than for that of thick corium specimens, but as the thickness of the split is decreased, the tensile strength of grain specimens decreases less rapidly than

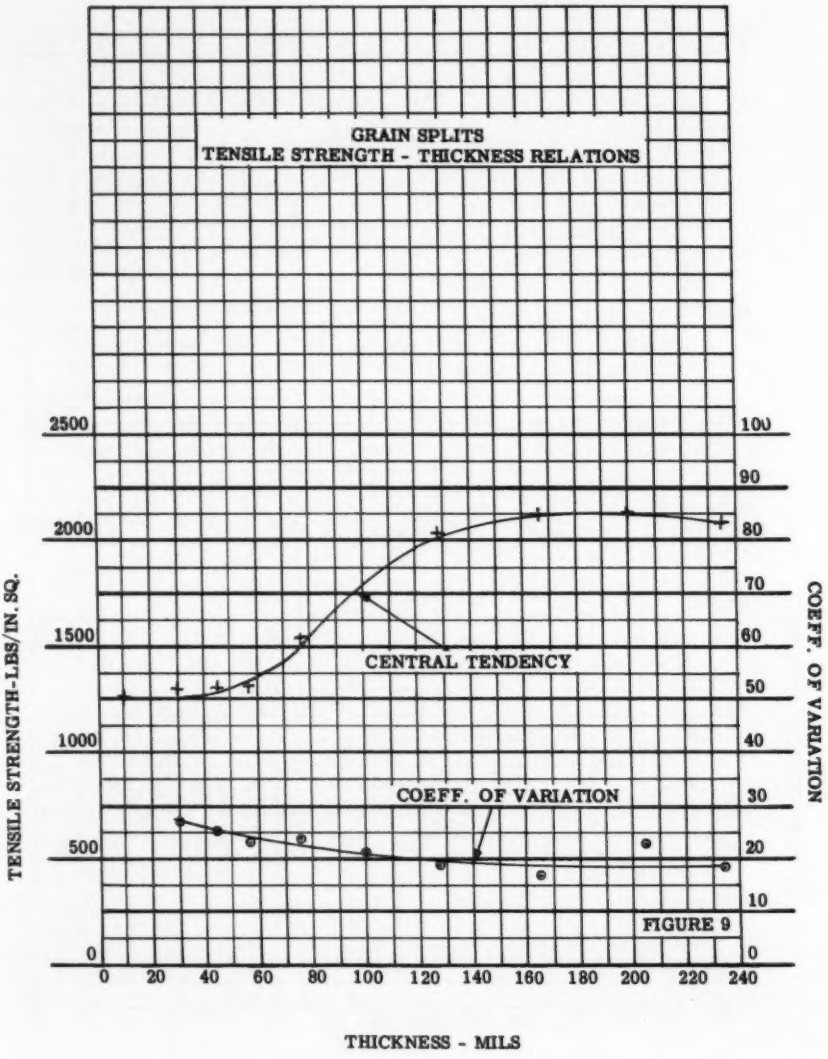


FIGURE 9

that of corium specimens, and grain splits as thin as 5 mils have a tensile strength of nearly 1000 p.s.i.

Tests on Retanned Splits

The above results were based on unfinished, lightly fat-liquored, chrome

tanned splits. The variations in the data may have been large because the specimens were cut from all parts of a rough, unfinished skin. It appeared possible that the conclusions drawn from such a test would not apply to a finished leather such as Army grade vegetable retanned upper leather. To check this point, the following test was made.

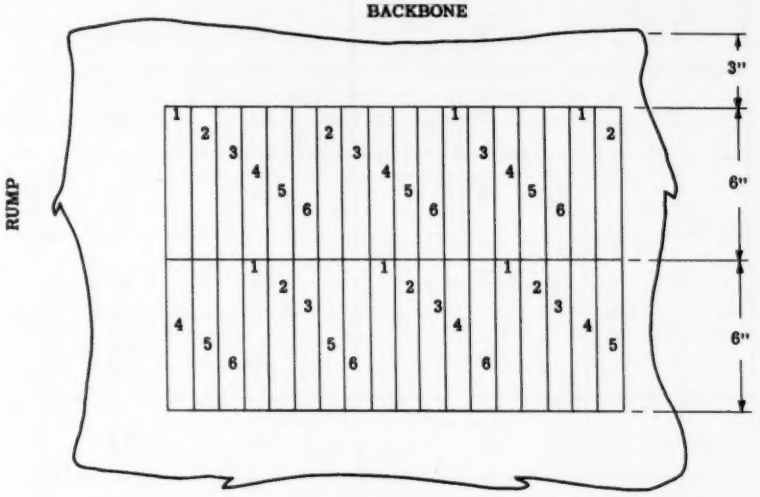


FIGURE 10

Test Specimens

In order to obtain the most uniform set of specimens which could possibly be cut, 36 pieces 1″ x 6″ were cut from the bend section of a single hide of Army retanned upper leather with the long axes of the pieces normal to the backbone. The original thickness of the leather averaged 86 mils, and varied between 83 and 90 mils.

The specimens were grouped as shown in Figure 10 with all the No. 1 specimens forming Group No. 1, and the No. 2 specimens forming Group No. 2, etc.

The pieces were split into a corium split and a grain split as shown in Table III.

Tensile specimens were cut, measured, and tested in accordance with the A.L.C.A. Method for Tensile Strength.

Results

Retanned Corium Splits

The breaking load in pounds per inch of width was calculated for each

TABLE III

GROUP	NUMBER OF SPECIMENS	THICKNESS OF SPLIT	
		GRAIN	CORIUM
1	6	86	None
2	6	61	25
3	6	47	39
4	6	35	51
5	6	28	60
6	6	14	72

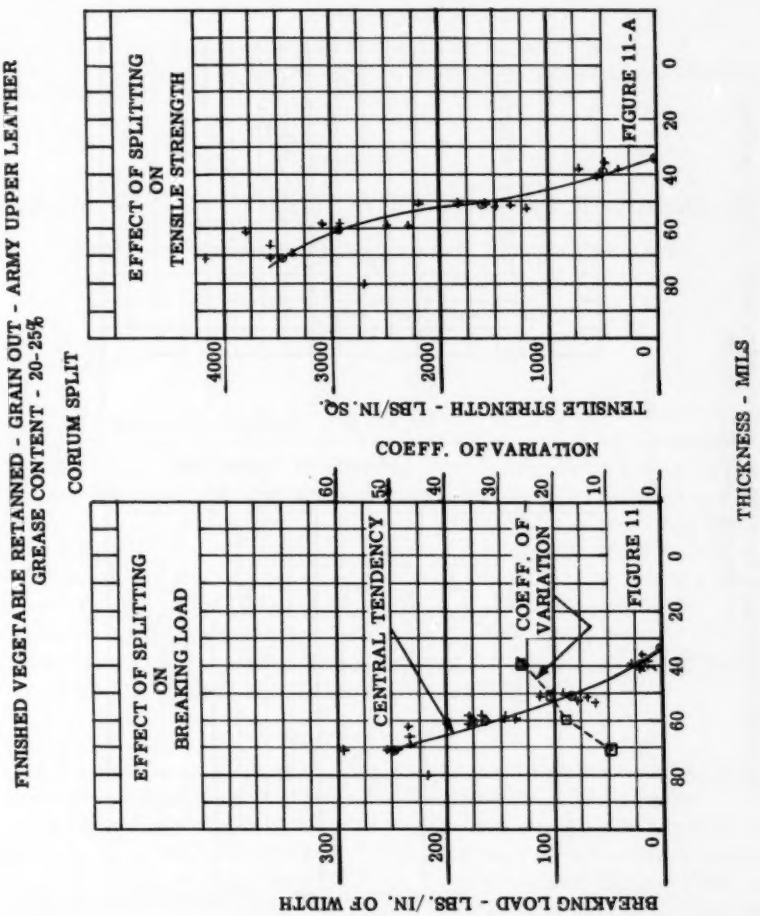
retanned corium specimen and plotted against its thickness in the scatter diagram of Figure 11. The central tendency and the coefficients of variation are shown on the same plot. The tensile strength of each specimen is plotted against its thickness in Figure 11-A.

The breaking load and tensile strength are higher for the corium splits of this leather than for chrome tanned corium splits of the same thickness, but the shapes of corresponding curves are similar and the intercepts on the thickness axis are nearly the same, at approximately 30 mils, for the two leathers.

The coefficients of variation are lower for retanned corium splits than for the chrome tanned corium splits varying from 10 to 25 per cent for the retanned split, as compared to 22 to 75 per cent for the chrome tanned splits.

Retanned Grain Splits

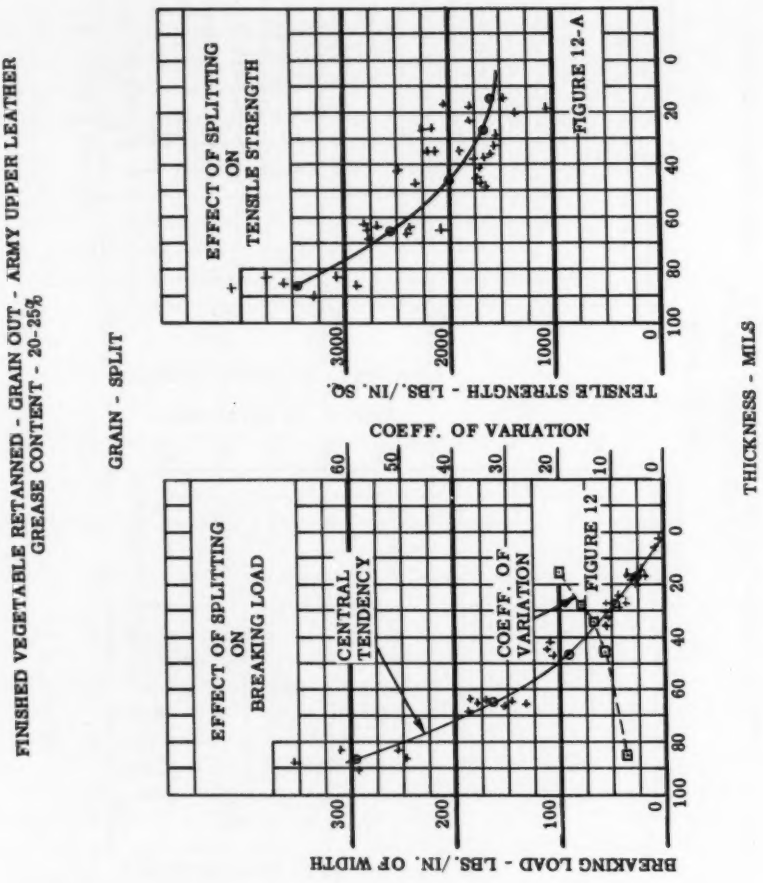
The breaking load, tensile strength, and coefficients of variation for the grain splits are plotted against the thickness in Figure 12 and Figure 12-A. The breaking load and the tensile strength curves are the same general shape as the corresponding curves for chrome tanned grain splits over the thickness range of 30 to 100 mils. Thin splits of the retanned leather and the



chrome tanned leather have approximately the same tensile strength, but as the thickness is increased, the retanned leather becomes much stronger.

As in the case of the corium splits, the coefficients of variation for the tensile strength of retanned grain splits are less than for the chrome tanned splits.

The similarity between the central tendency curves for the rough unfinished chrome tanned leather and the carefully selected samples of finished retanned leather suggest that the changes which occur in the tensile properties of leather with a change in thickness are inherent in the skin and are influenced only slightly by the tanning processes.



The results from both leathers show the extreme variability of leather as compared to other materials. The coefficient of variation for specimens of leather selected for the greatest possible uniformity is 10 per cent or greater as compared to 1½ per cent to 3 per cent for metals, plastics, textiles, and other manufactured products. If a product with such wide variability is to be used successfully and economically in industrial applications, the nature and magnitude of its variations must be known so that allowance can be made for a predictable number of inferior parts.

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Tannin Analysis Method - Problems and Modifications*

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Summary

The A.L.C.A. Standard Method for tannin analysis gives reproducible results for vegetable tans but not for lignosulfonate tanning products. A modification of this method substituting Waring blendor agitation for five minutes instead of the standard ten-minute shake procedure gives a more factual value for lignosulfonate as shown by depletion of methoxyl in the non tannin solution, and maintains the correct values for vegetable tans.

Lignosulfonate tanning materials, bisulfited vegetable tans, and, to a lesser extent, vegetable tans replace sulfate groups in chromed hide powder. This is indicated by a higher sulfate content in the non tannin solution than is present in the analytical strength solution. As a result, the calculated tannin uptake is too low unless proper correction is made.

Introduction

It is of obvious importance to the tanner to have a practical and accurate method for determining the tannin content of all the tanning agents in the various processing stages in his plant. The hide powder shake method is generally accepted in this country. Variables have been eliminated and in its present form the Standard A.L.C.A. Tannin Analysis Method gives reproducible results, correlating with tannery findings when applied to vegetable tans. However, it is recognized by this association that the standard method, when applied to lignosulfonates and syntans, gives unsatisfactory results. With these materials, experienced analysts obtain results which, even with the strictest adherence to the standard method, show considerable differences as illustrated by the association's test panel results some time ago [1].

Evidence indicates that the conditions of the standard method are not suitable for complete absorption of the tannins in lignosulfonate products. The non tannin solution by the standard method always contains some lignosulfonate which, under proper tanning conditions, can be absorbed by hide

*Presented at the Golden Jubilee Meeting of the A.L.C.A. in Cincinnati, Ohio, June 8, 1953.

powder. There is now ample tannery evidence that lignosulfonates have higher tannin content than determined by the present standard method. The following example will illustrate this: Seven hundred pounds of chromed wet shaved hides were drum tanned with a given amount of vegetable tan of known purity. Another seven hundred pounds of hides of the same lot were drum tanned with a lignosulfonate extract which contained 75 per cent lignosulfonate by methoxyl determination but only 41 per cent tannin by the standard method. The lignosulfonate product was added on the basis of 75 per cent tannin content in an amount equivalent to the vegetable tannin. Resulting leathers showed 30 degrees of tannage in both cases. If the 41 per cent value determined by the standard method were correct, the leather in the second drum would have had only 17 degrees of tannage.

This report describes modifications in the tan analysis method which give results consistent with tannery practice for lignosulfonate as well as vegetable tanning agents.

Experimental

Previously reported studies [2], [3] and [4], have shown that tannin values obtained by the reaction of lignosulfonate with hide powder are influenced by time, temperature, concentration, and hydrogen ion concentration. Since it was desirable to retain as many of the standard method conditions as possible, the study centered on the effect of temperature and time on lignosulfonate absorption. It was found that 95 per cent of the lignosulfonate was absorbed by the hide powder when the temperature reached 40–45° C. This temperature is impractical for the standard procedure with the shaker. However, it was found that standard amounts of hide powder and tan solution could be reacted very conveniently in a Waring blendor because the reaction can be started at room temperature and there is then sufficient heat developed by the blendor action to reach 40–45° C. Five minutes are required for the hide powder to absorb 95 per cent of the lignosulfonate. This

TABLE I

Comparison Between the Standard Shake Method and the Waring Blendor Modification

	(grams tannin per 100 grams dry product)	
	Shake Method	Waring Blendor Modification
Lignosolfonate Products		
Precipitated lignosulfonate	41.4	66.7
Sulfite liquor lignosulfonate	42.3	46.0
Vegetable Tans		
Wattle	73.8	73.8
Chestnut	57.8	57.8
Quebracho	74.6	74.2

modification has slight or no effect on vegetable tan analysis and gives reproducible results when five minutes agitation time is observed. The results were compared with those obtained by the standard shake method. Typical results are shown in Table I, illustrating that the Waring blendor modification gives higher tannin value for lignosulfonate products but practically identical results for vegetable tans.

When a lignosulfonate is reacted with chromed hide powder, the amount absorbed can be calculated from the difference in methoxyl content between the analytical strength solution and that of the non tannin solution. This calculated lignosulfonate value was greater than the tannin value determined by the difference in dry solids content of the two solutions. The discrepancy could result if part of the hide powder dissolves and is weighed with the non tannin solids.

Detailed analysis of the non tannin solution identified this solubilized hide component as inorganic sulfate (SO_4), evidently exchanged from basic protein groups or chrome-complexed sulfate groups in the chromed hide powder by the lignosulfonate. It was found that vegetable tans also displaced sulfate groups from chromed hide powder as shown by a higher sulfate content in the non tannin solution than in the analytical strength solution. This displacement is particularly pronounced with sulfited vegetable tans and occurs in the A.L.C.A. Standard Method as well as the Waring blendor modification. It contributes considerable error in all tan analysis with chromed hide powder. To obtain true tan absorption, results must be corrected by the amount of sulfate displaced from the hide powder. Table II gives the standard purity values and the values after correcting for sulfate displacements when analyzed by the Waring blendor modification.

TABLE II

Effect of Sulfate Displacement on Tannin Values
Waring Blendor Modification

	(grams tannin per 100 grams dry product)		
	As Determined	Corrected for Displaced SO_4	Difference
Quebracho	74.2	75.1	0.9
Chestnut	57.8	58.7	0.9
Cutch	69.3	71.3	2.0
Wattle	73.8	75.7	1.9
Sulfited quebracho	84.0	88.3	4.3
Precipitated lignosulfonate	66.7	72.2	5.5
Sulfite liquor lignosulfonate	46.0	51.5	5.5

Table III gives corresponding results with the A.L.C.A. Standard Shake Method.

TABLE III

Effect of Sulfate Displacement on Tannin Values
Standard Shake Method

	(grams tannin per 100 grams dry product)		
	As Determined	Corrected for Displaced SO_4	Difference
Quebracho	74.6	75.5	0.9
Chestnut	57.8	58.8	1.0
Cutch	69.4	71.0	1.6
Wattle	73.8	75.5	1.9
Sulfited quebracho	83.8	87.9	4.1
Precipitated lignosulfonate	41.4	45.4	4.0
Sulfite liquor lignosulfonate	42.2	47.3	5.1

In this study, the displaced sulfate is calculated as SO_4 and is determined as the difference between sulfate in the analytical strength solution and the non tannin solution. While such analyses are readily carried out by precipitating with $BaCl_2$, filtering, igniting and weighing of the resulting $BaSO_4$ precipitate, the time involved makes it desirable either to eliminate sulfate displacement or simplify the method of correcting for it. These possibilities have been explored but no satisfactory solution has been found. They are briefly described for the purpose of stimulating further ideas and avoiding duplication of unsuccessful ones:

Sulfate displacement was avoided by using unchromed hide powder, but the tannin values for both vegetable and lignosulfonate products were low. This is due to some solubilization of hide substance and to decreased hide powder reactivity.

The chrome-alum solution was boiled for one hour prior to treating the hide powder with it. This produced a decrease in pH from 3 to 1.7, indicating release of sulfuric acid along with olation. The resulting sulfate displacement was no less than when standard hide powder chroming was used.

Chromed hide powder was leached with oxalic acid to replace the sulfate group. This organic acid is reported [5] to be more resistant to replacement by tannins. However, the sulfate still remained high in the non tannin solution.

When chromed hide powder was leached with sodium bicarbonate prior to use in tan analysis, the sulfate displacement was decreased but the hide powder had also reduced reactivity due to this pretreatment and was therefore unsuitable for tan analysis.

Treatment of the non tannin solutions with various sparingly soluble sulfate-removing agents, such as barium and strontium carbonate, and activated alumina [6], was practically ineffective at the pH of the non tannin solution.

Conclusions

1. Tannin values for lignosulfonates will coincide with tannery results by substituting the five-minute Waring agitation for the ten-minute shake procedure in the A.L.C.A. Standard Method for tannin analysis.
2. A hitherto unknown or neglected error in the standard method results in a lower tan value for all tanning materials, but particularly for sulfited extracts and lignosulfonates. An analytical procedure for compensating for this error is given, but a more convenient means for eliminating the error is desirable.

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Determination of Copper as a Minor Constituent of Vegetable Extracts

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Inquiries from leather chemists have suggested that a review of methods for the determination of copper as a minor constituent of tannery materials would be desirable. The American Leather Chemists Association has a provisonal method [1] which employs potassium ethyl xanthate to develop a color proportional to the amount of copper present. However, this does not seem to be completely acceptable. Thus, one testing laboratory has informed us that "the method for copper needs further investigation as it is very difficult to match the color produced, due to weakness of color and cloudiness." This and other similar comments prompted this survey.

The amount of copper commonly found as a minor constituent of tannery materials is a few hundredths of a per cent. This level of copper is most conveniently determined by colorimetric methods. Hence, the available colorimetric methods have been examined in this survey. Sandell [2] was the primary source of much of the information contained in this article, and is particularly valuable for his discussion of the factors influencing the precision of colorimetric methods generally.

Numerous colorimetric reagents have been proposed for copper. Muller and Burtsell [3] in 1940 made a comparative study of many colorimetric methods for copper. They used a filter photometer, and were particularly concerned with the agreement of the colors produced to Beer's law, i. e. that the optical density is directly proportional to the amount of copper present. Sandell [2] reviews a few of these methods critically, and the more recent literature has been searched for more specific copper methods.

This literature review suggested that the following reagents be considered in analyzing vegetable extracts for copper.

Trivial Name	Chemical Name	Critical References
Carbamate	Sodium Diethyl-dithiocarbamate	2, 4
Cuproine	2, 2[1] Diquinoline	5, 6
Dithizone	Diphenyl thiocarbazone	2
Neo-cuproine	2, 9 Dimethyl, 1, 10 phenanthroline	7
Rubeanic Acid	Di-thio-oxamide	8, 9
Xanthate	Potassium ethyl xanthate	1, 10, 11

The carbamate method for copper depends upon the formation of a chelate complex which is formed with cupric salts. The complex is sparingly soluble in water, but soluble in several organic solvents. Lacoste et. al. [4] show that the method is far from specific for copper, being applicable also to the determination of bismuth, cobalt, chromium, iron, nickel, and uranium as well. However, the colorimetric systems obey Beer's law, and the colors formed are rather stable. The literature contains two common methods to secure the colored solution of the complex for measurement. Colloidal stabilizers such as gum arabic are useful in very dilute solutions. However, a liquid-liquid extraction with chloroform or carbon tetrachloride is the most common. We have developed a method in which the solution is brought to pH 9.1 with buffer and then the color is developed. The complex is solubilized by the addition of sufficient acetone to make the colored solution 50 per cent acetone by volume. The yellow-brown color is read at 440 millimicrons, or compared visually to the standards. It must, however, be clearly realized that this method is not specific for copper, so that interferences must be eliminated before the test is conducted. The test is very sensitive, detecting 1 part of copper per 100 million parts of solution.

The cuproine method is a very specific method for cuprous copper. It produces such an intense color, deep purple, that even high concentrations of colored ions such as nickel, iron, or cobalt do not interfere. It is sensitive to 0.02 microgram per ml. or 1 part of copper per 50,000,000 parts of solution. The color is customarily extracted from the aqueous phase by the reagent in iso-amyl alcohol. The color obeys Beer's law, is stable and is formed over the pH range 2 to 9. It is therefore a very desirable method for the analysis of small quantities of copper.

Dithizone is the general heavy metal reagent par excellence for trace metal analyses. Seventeen different metals in valence states from 1 to 3 form highly colored metal dithizonates. Specificity of the reaction is controlled by careful control of the conditions of color development and extraction. In the presence of 0.1 *N* mineral acids, copper forms a red-violet color but bismuth, palladium, gold, silver and mercury will interfere. The reagent itself is colored, being a dichroic green in chloroform or carbon tetra-chloride. This color requires careful control of the wave length at which the copper color is read. However, readings at 510 millimicrons (red filter) can be linear with respect to the copper concentration. The method will detect as low as 0.1 part per million in carbon tetrachloride.

The work of Hoste [5] on cuproine designated the functional group

$$CH_3 - \underset{|}{C} = N - \underset{\|}{C} - \underset{\|}{C} - N = \underset{|}{C} - CH_3$$

as a copper specific group. Smith and McCurdy [7] used this information to select neo-cuproine for study as a copper-specific colorimetric reagent. The method is sensitive to as low as 0.05 parts per million cuprous copper, and obeys Beer's law. The color is stable, and may be read at 454 millimicrons. It is specific for copper among all the cations, and anion interference results only from those ions which interfere with the hydroxylamine reduction of cupric salts to cuprous salts.

Rubeanic acid has been suggested for the determination of copper in magnesium alloys [8] and steel [9]. Nickel, ferrous iron, cobalt, silver, mercury, lead, and aluminum interfere in the method. However, malonic acid may be used to control some of these interferences. The color obeys Beer's law and may be read between 650 and 675 millimicrons.

The xanthate method, specified by the A.L.C.A. Committee on tannin analysis for copper in vegetable tanning extracts [1], is considered by Sandell as an alternate to the carbamate method. This was also shown by Conn et. al. [11] who noted its lower sensitivity in comparison to the carbamate method, as well as the difficulty from the development of turbid colors. They conclude that only at pH 7 at a copper concentration of 0.005 to 0.020 mg. per 25 ml. can turbidity be minimized. King and Etzel [10] note that nickel interferes by giving a similar color, and that other salts especially iron, influence color development and turbidity. They emphasize that the reagent salt must be recrystallized frequently, and the solutions used promptly to avoid turbidity. The color does not have any characteristic adsorption maximum in the visual range, so it is a poor method for instrumental colorimetry. In visual colorimetry, the standards must be carefully developed to be identical to the unknown, even to the extent of having the same amount of excess reagent. Hence, the method of titration to a colorimetric end point is advisable for visual accuracy.

The dithizone method in colorimetry is particularly useful as a separatory and isolation technique for traces of copper, rather than being a specific colorimetric assay for copper. Further, the dichroic red-green color of the reagent makes the red to yellow colors of the metal dithizonate difficult to detect in visual colorimetry. Thus, the method, though capable of precise estimation of traces of copper, did not seem especially suitable for our purpose. However, the other five methods were examined for their use as a copper assay for tanning extracts.

Experimental Procedures and Results

The ashing method specified by the A.L.C.A. for copper and iron in tanning extracts specifies an ashing temperature not exceeding 600° C., and the use of a porcelain crucible with a clean, intact glaze. These precautions were followed in this work. However, two different procedures were followed in the solution of the ash. First, the ash was dissolved by boiling it with 70 per cent perchloric acid. This will put most metal ions into solution and insure that the copper would all be divalent. Second, the ash was dissolved in hydrochloric acid and then made slightly alkaline with ammonium hydroxide. The precipitated iron and aluminum hydroxides were filtered off in a fritted glass crucible. Then, the filtrate was used for copper analyses. In this method, the copper was not necessarily forced to be divalent, although this was most probable. Of course, some possible interferences had been eliminated, but at the possible loss of copper by occlusion in the precipitate.

On the basis of the information in the literature, these solution techniques seem adequate. However, for very precise work some consideration should be given to destruction of the organic matter and the simultaneous solution of the metal traces by the use of mixed acids, such as nitric and sulfuric followed by perchloric acid. This would prevent any possible copper loss by fusion with crucible walls or loss in transfer from the crucible.

The extract analyzed was an imported chestnut extract sample supplied by a tanner because it seemed to contain a high copper content. All colorimetric analyses, except the visual A.L.C.A. xanthate method, were performed on a Beckman DU Spectrophotometer. However, it should be clearly understood that these methods would also be usuable with a filter photometer or even visual colorimetry. We used the spectrophotometer because it was the most precise and convenient method of colorimetry available to us.

Table I summarized the experimental details for the four methods taken from the literature as they were applied by us. The refrences cited will give the general method while the table emphasizes certain of the critical points in the procedures. The data secured from these procedures applied to the imported chestnut extract thought to contain copper in large quantities appear in Table II.

It will be evident from these tables that all five of the methods are applicable to the purpose. The xanthate method has not given the same results on the

TABLE I

The Laboratory Details in Colorimetric Assays
Copper in Tanning Materials

Methods Detail	Colorimetric Method			
	Carbamate	Rubeanic Acid	Cuproine	Neo-Cuproine
Literature Reference	2,4	8	12	7
Reagent Strength	0.1% aq. carbamate	0.1/g1. acetate Soln.	0.02% Iso—Amyl Alc.	0.25% inEt-OH H_2O
Reductant	None	None	Hydroryl-amine	Hydroryl-amine
Buffering Solution	NH_4 Citrate-pH 9.1	NH_4 Malonate	pH2 to pH9	Na Citrate-pH 4 to 6
Color Extractant	None	None	Reagent	Iso-Amyl Alcohol
Color Solvent - Reading	50-50 Acetone H_2O	Reagents	Reagent	Iso-Amyl Alcohol
Milimicrons for Reading	440	675	546	454
Color Density-0.1 mg./100 ml.	0.185	0.064	0.093	0.112
Color Stability	Read 1 to 3 Hr.	Several Hours	72 Hours	Days

TABLE II

Chestnut Extract Analysis Expressed as
Copper Content in Per Cent Cu By Weight
Extract Contained 90.6% Solids, 1.5% Ash, 0.015% Fe.

Colorimetric Method	Method of Ash Solution	
	Perchloric Acid Oxidation	HCl-NH_4OH Treatment
Xanthate	0.040	0.060
	0.040	0.060
Carbamate	0.056	0.054
	0.055	0.053
Rubeanic Acid	0.057	0.053
	0.058	0.054
Cuproine	0.061	0.059
	0.054	0.059
Neo-Cuproine	0.060	0.053
	0.060	0.054

perchloric acid digest, perhaps because of the greater acidity of this digest, with a resultant influence on color development and turbidity. However, it must be realized that it has been the experience of those using the xanthate method that it is not as reproducible as is desired. The four alternative methods have given results which seem as reproducible as can be expected from colorimetric assays at these low levels of copper. It is noted that the results

from the perchloric acid oxidation tend to be slightly higher than those from the hydrochloric acid—ammonium hydroxide procedure. This could result from either iron interference in the perchloric acid digestion samples or loss of copper in the iron separation with ammonium hydroxide. Little evidence is available from these few data on this point. However, the fact that the very specific neo-cuproine method gives higher results on the perchloric acid digest would seem to support the latter explanation that copper was lost during iron removal.

The four alternate methods each have their specific advantages. The carbamate and the rubeanic acid methods are methods in which the color is developed and read in an aqueous system. This is more convenient than the cuproine and the neo-cuproine methods which require an extraction of the color with an organic solvent in a separatory funnel. On the other hand, the neo-cuproine color is very stable and specific for copper, these are factors worthy of consideration for industrial use. The carbamate method has proven to be the most sensitive in our hands, but its specificity is poor, and the particular solvent system we use to avoid the liquid-liquid extraction does not yield too stable a color system.

The neo-cuproine method is preferred by us as the most specific method, and therefore the most generally applicable method. The carbamate method is the least difficult method, and it is our second preference. Its greatest deficiency is the greater probability of interferences. The xanthate method is the poorest of the five methods in our experience. Extreme care is required to prevent cloudy colors, and the color system is not applicable to efficient instrumental colorimetry. For visual colorimetry any of the four alternate methods are as adaptable as the xanthate method, the colors ranging from the green of the rubeanic acid color, the purple of the cuproine color to the yellow of the carbamate method.

This comparison of the several methods by a single laboratory on one extract can not select the best method for general use. This article is published in the hope that others may use the methods, and thus be able to furnish information which will permit the final selection of the best method.

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The Role of Lanthionine in the Unhairing Immunization Phenomena*

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It has long been known that the use of sulfides as accelerators in the lime liquors, used for unhairing skins and hides, decreases the total time needed for unhairing. If the skins or hides are treated with the lime solutions for a few hours before the sulfide is added, the acceleration due to the sulfide is reduced. This phenomena was termed immunization by Hirsch [1] who claimed it began at a pH of 12.

Alkali treatment of wool, hair, and hide has been studied by many researchers. Crowder and Harris [2] have investigated the alkali degradation of wool and found that approximately one-half of the sulfur is easily removed from the wool, and that the sulfur is inorganic in character. Merrill [3] concluded that a reaction between keratin and SH^- ion takes place and alters the structure of the protein so that the residues are more readily attacked by the OH^- ion.

Theis and Blum [4] worked on alkali treated human hair and reported that for values less than pH 12, the sulfur content was only slightly acted upon. When the pH was increased to beyond 12.5, the alkaline solubility of the hair was decreased to a value approaching 50 per cent of the original sulfur content of the hair. The presence of sulfides or cyanides in the unhairing solution increased the solubility of the hair substance, but pretreatment of hair with a lime solution before the addition of accelerators materially reduced the ability of the hair to dissolve, thus immunization of the hair was accomplished [4].

*This paper is abstracted from a thesis presented by Mr. Shaw to the Graduate School of Arts and Science June, 1953, in partial fulfillment of the requirements for a master of science degree.

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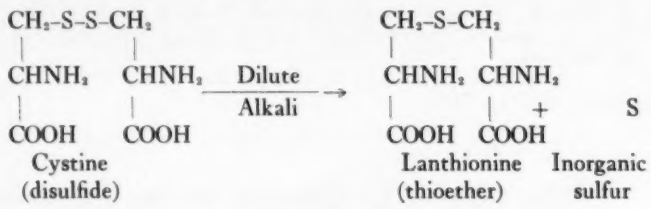
Horn, Jones and Ringel [5] reported the formation and isolation of a thioether amino acid from dilute alkali treated wool and it was named lanthionine (β,β′—Thiodialanine), $(COOHCHNH_2CH_2)_2S$. Using cystine as an example, the reaction could be represented as:



Since almost all of the sulfur in undegraded wool or hair can be accounted for as cystine sulfur, it appears that lanthionine is a product of the reaction of the cystine in wool and hair with alkali [6, 8].

It was first suggested by Hirsch [1] that the breakdown of the labile disulfide linkage, R–S–S–R, in the keratin into the thioether linkage, R–S–R, by the action of alkali, could be the cause of immunization. The thioether linkage would be much more resistant to strong sulfide solution or other alkali degradation.

There have been no reports of the formation of lanthionine with lime or under commercial unhairing conditions, although Hirsch [1] as well as Windus [15] have postulated that such a reaction could take place and might possibly account for the immunization phenomena. This experimentation was undertaken to investigate the possibility of lanthionine formation under unhairing conditions, its possible connection with immunization, and the further elucidation of the unhairing mechanism.

I. Experimental

Preparation of Samples

The hair and sections of hide used in the experimental work were taken from cattle hides and calf skins obtained from a local packer shortly after slaughter. The hides were washed, cut into strips, and frozen until ready for use, at which time they were allowed to thaw and then soaked for a 24 hour period to rehydrate them. The steer hair used was degreased by extraction with alcohol and acetone, and air-dryed. For the sections used as epidermal split, the hide was split at a point below the base of the lowest hair pockets. The hair on these sections was cut off at approximately one-quarter of an inch from the outer surface of the epidermis by the use of animal clippers.

Elemental Analyses on Lanthionine Isolates.

The sulfur analyses were made by the micro-Carius method [19], and nitrogen analyses by the semi-micro modification [18] of the Kjeldahl-Gunning method

as used by Buechler and Lollar [17], with the use of cupric sulfate as the catalyst during the digestion period.

Demonstration of Immunization.

The immunization phenomenon was observed and demonstrated on fresh steer hides by the following experiment. Pieces of fresh soaked steer hide two by four inches, (2″ x 4″) were treated with:

(a) lime only
(b) lime, sulfide added later.
(lime only, for 3 hours, then 0.3% Na_2S)
(c) 0.1% Na_2S and lime.
(d) 0.3% " " "
(e) 1.0% " " "

A saturated lime solution with 12 per cent excess lime on the stock weight basis was used with a 4 to 1 ratio of solution to stock. The per cent of sulfide is also expressed on the stock weight basis. The solutions were agitated many times daily. After a four day liming period at 22–26° C., the hair was removed readily from samples (c), (d), and (e), and in (e) the hair showed signs of the strong alkali attack. The hair was removed much less readily and with approximately the same degree of difficulty in (a), and (b), the lime only and the lime delay sulfide samples.

The same process was repeated using larger areas of epidermal split which had been split from the corium at a point below the hair pockets. Epidermal splits were used to concentrate the hide portion containing keratins. Sample (b) was treated with lime only for two hours, then 0.3 per cent sulfide added, while the other four sections were treated as designated above. Samples (c), (d), and (e) were unhaired fairly readily after a three day liming period while in (a) and (b) less readily after four days liming, but again with the same approximate degree of difficulty.

Isolation of Lanthionine

Lanthionine has been isolated from many cystine containing substances [5, 21] after treatment with solutions of sodium carbonate, sodium hydroxide, or sodium sulfide. Horn and Jones [21] postulated that it should be obtained from most proteins which yield cystine upon acid hydrolysis and attributed the formation of lanthionine to be due to an alakli effect rather than due to any particular alkali used. They found, however, that when a strong alkali solution such as *N* (normal) NaOH was used, all wool was dispersed and cystine was obtained instead of lanthionine.

Calcium hydroxide was not one of the alkalies used and reported in the literature although its low solubility produces a dilute solution of a strong alkali which has been observed necessary for lanthionine formation. Our

experimentation was designed to determine whether lanthionine formation could be accounted for during liming conditions.

Five hundred gram samples of fresh steer (200 grams) and calf (300 grams) epidermal split, with the hair clipped close and removed, were used as test samples to check for lanthionine formation. The great majority of the hair was removed, and thus the majority of the eukeratin (high cystine content), so as to focus our attention upon the epidermal area where unhairing is believed to occur.

It had previously been reported [22] that no lanthionine could be obtained from cow hair unless it had been treated with alkali. Shimomura [23], however, reported the isolation of a denatured form of lanthionine from horse hoof without previous alkali treatment.

To be sure that lanthionine was not naturally occurring in the hair used, the first sample was used as control and processed as fresh stock without alkali treatment. The second sample of closely clipped stock was limed with lime only for 2.5 to 3 hours, then sodium sulfide (0.3 per cent) was added and liming continued for an additional 13 to 13.5 hours until a total of 16 hours had been reached. The third sample was limed using 0.3 per cent sodium sulfide and calcium hydroxide (lime) simultaneously for 16 hours. The lime was a saturated solution with 12 per cent excess on the stock basis and a 4 to 1 ratio of solution to stock. The sulfide was 0.3 per cent on the stock basis.

The entire epidermal splits were hydrolyzed in concentrated HCl, the solutions decolorized using the same amounts of decolorizing agents, and the lanthionine isolated by Horn, Jones and Ringel's method [5] using the modification of Mizell and Harris [12].

From the two alkali treated samples, the second and the third of closely clipped epidermal split, identical amounts of lanthionine within experimental limits were isolated. The yield of lanthionine represented practically the entire amount of product isolated before purification. The purified lanthionine was 0.136 grams from the sample which had lime plus lime sulfide treatment, and 0.141 grams from the sample given the lime sulfide treatment for the entire period. The lanthionine products showed the following analytical characteristics in comparison to actual values for lanthionine:

	Actual Values for Lanthionine $C_6H_{12}O_4N_2S$	Lime Delay Sulfide	Lime Sulfide
Softening	meso-270(5, 7)	270 (some)	270
Decomposition	meso-279(22); 304 (5); 308 (7); d,l 283–284 (16)	281–283	282–284
Per Cent Nitrogen	13.46	13.43	13.37
Per Cent Sulfur	15.41	15.36	15.62

No trace of lanthionine could be found from the first sample, the control epidermal split which had no alkali treatment, after it was processed and treated under the conditions used for lanthionine isolation.

Although the immunization phenomena has been said to take place in a much shorter time than two to three hours, this time interval of two to three hours was used to insure, that if lanthionine were formed, there would be enough formed to isolate it quantitatively by semi-micro adaptation of the normal procedure.

Steer hair was used to check our findings of lanthionine formation, and to verify that the first three hours of liming (with only lime) played a significant role in lanthionine formation in the experiment described above. Two dry, ten gram samples of washed and degreased steer hair were treated using an alkali treatment process somewhat similar to the flow method suggested by Mizell and Harris[12] to obtain greater possible yields. This adaptation was considered necessary, for our liming conditions for alkali treatment were not as radical as the alkali treatment previously used[5, 12] for the formation of lanthionine.

One sample was treated with a saturated lime solution (plus excess) for three and one half hours and the other sample with lime sulfide for an identical period of time, by allowing fresh solutions at 26°C to be continuously in contact with the hair and thus to wash reaction products away from the fibers and keep secondary reactions at a minimum. The flow of fresh solutions was accomplished by siphoning the fresh alkali solution into the bottom of the container and removing the spent solutions from the top at approximately the same rate. The hair was then hydrolyzed and lanthionine isolated as before.

Similar amounts of lanthionine, within limits of experimental error were found; 0.263 grams from lime only and 0.252 grams from lime sulfide. The lanthionine gave the following characteristic values:

	Actual Values For Lanthionine $C_6H_{12}O_4N_2S$	Lime	Lime Sulfide
Softening	270 (5)	270 (some)	271
Decomposition	283–284 (16)	284–286	283–284
Dibenzoyl Derivative	195–198 (16)	195–197	194–196
Per cent Nitrogen	13.46	13.49	13.47
Per cent Sulfur	15.41	15.29	15.37

II. Determination of Lanthionine

Colorimetric

The procedure of Sullivan and Folk[20, 24] for the quantitative determination of lanthionine was tested. This procedure consists of the conversion of lanthionine to cysteine by the use of NaCN–CNBr reagent, and the deter-

mination of the formed cysteine colorimetrically. However, the results secured were unsatisfactory, since it was impossible to separate the natural cysteine from the formed cysteine or to secure quantitative conversion of the lanthionine to cysteine. Hence the method was abandoned.

III. Discussion

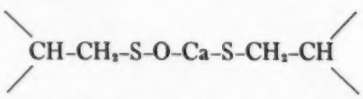
The results obtained would indicate that lanthionine formation is taking place during the course of unhairing when the hides are treated with lime alone or in the presence of an accelerator, sodium sulfide. They would also indicate that lanthionine formation is not the cause of immunization for approximately equal amounts were found when sodium sulfide was both present and absent.

The yield of lanthionine obtained was much lower than was obtained by Horn *et al*[16] on the human hair; however, human hair is richer in cystine than cattle hair[28]. Further, our experimental conditions, involving a much lower temperature and a longer duration of alklai treatment, could result in lower yields.

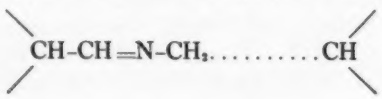
A probable mechanism of unhairing with the reducing agent sodium sulfide, was set forth by Merrill[3], and by Windus and Turley[29] as involving both reduction of the disulfide linkages of the cystine of the keratin and hydrolysis of the other linkages by the alkali present in an unhairing liquor. Merrill showed that in the presence of sulfide, the effect upon the hydrolysis produced by increasing the pH value of the solution was very much greater than in the absence of sulfide, and therefore that a reaction between keratin and SH^- ion takes place and alters the structure of the protein so that the residues are more readily attacked by the OH^-ion.

Theis and Blum[30] showed that the SH^- ion is not sufficient for unhairing but that the OH^- ion is also necessary. As_2S_3 was used and it was postulated that $Ca(HS)_2$ was formed, and they found that as the pH decreases due to increase of $Ca(HS)_2$, actual unhairing was retarded.

McKay[31] demonstrated the presence of un-ionized calcium in hair which had been immersed overnight in lime water. He states that in the absence of sulfide the initial hydrolysis of the disulfide bond is followed partly by the formation of metalic links,



suggested by Marriott, and also in part by the loss of H_2S from sulfide groups, followed by the linking of the residual aldehyde with an amino group to give:



This type of new link was suggested by Phillips[32]. Both these links would be stable to alkali and reducing agents, and thus McKay postulates that their formation would account for the failure of sulfide to accelerate unhairing on hides previously immersed in straight lime.

Although the hair undergoes some alkali attack during liming, the unhairing phenomena are known to involve the epidermis of the skin as well as the hair, for the epidermis is also removed during the unhairing. Wilson[33] has stated that unhairing by lime takes place in the epidermis both with or without the presence of sodium sulfide and it has been demonstrated[33, 34] histologically that the epidermis is the area of active breakdown during unhairing. The epidermis extends down the walls of the hair follicles, and when the more sensitive epidermis and hair roots are affected the hair is also loosened.

Semenova[36] has shown that when hides are treated with saturated lime solutions, or a high concentration of monethanolamine and lime, the loss of sulfur of the epidermis is significantly greater than the losses of sulfur of the hair. Buechler and Lollar[17] have shown that a distinct difference exists between the chemical composition of cattle hair and epidermis, with epidermis being much lower than hair in cystine and total sulfur, and higher in methionine. They also found disulfide that could not be accounted for as cystine. They suggested the possibility that the breaking of disulfide bridges is not a necessary adjunct to unhairing, considering the histological demonstration that the epidermis is the chief point of attack during unhairing and that it contains only a very small amount of cystine.

The work of Roddy and O'Flaherty[35], based on visual examination of ash patterns (micro-incinerated section), showed that it required 12 hours for lime to completely penetrate calf skin, with continuous uptake of lime occurring for three days. Samples of skin treated in lime plus sharpeners (arsenic sulfide, sodium sulfide, and dimethylamine) had complete penetration of the calf skin in two to three hours, with uptake increasing for three days. In all cases penetration by alkali was entirely from the flesh side.

As fresh hide was used in the present experimentation the penetration of lime into a fresh hide from lime liquor and lime-sulfide liquor before and after immunizing the stock with lime was studied by micro-incineration. The fresh hide is much more permeable to lime than the salt cured stock as judged by complete penetration of lime in two hours. The lime solution penetrated from the flesh side.

The lime-sulfide stock showed complete penetration in one hour. The lime penetrated both the grain and flesh sides in this case at an equal rate. The immunized stock was quite similar to the straight lime ash pattern. The lime-sulfide ash pattern was different at a corresponding time period.

A possible explanation for unhairing and the immunization phenomena, occurring when sodium sulfide is added after the lime, could be that lime alone, as it penetrates from the flesh side, combines with the protein, forming per-

haps calcium proteinate, which would be resistant to the effect of sharpeners. This phenomenon might be considered somewhat analogous to the case hardening effects occurring in vegetable tanning when too strong liquors are used, and penetration of tannin as a consequence is much slower. If alkalinity is increased by addition of sodium sulfide before the skins are added, lime becomes less soluble and thus less calcium proteinate forms and penetration through the stock is facilitated. The lime-sulfide system attacks the epidermal tissue from the corium side, cleaving the protein residues holding the epidermis which contain a small amount of disulfide bridges, and thus freeing the epidermis and hair.

It must also be recognized that the theory expressed by McKay[31] and discussed earlier may explain immunization also. This work can only indicate that lanthionine formation does not seem to play a major role in the phenomenon.

IV. Summary

Lanthionine was formed under unhairing conditions and was found in equal amounts both when lime alone acted upon the hair or epidermal area and when the lime sulfide solutions were used. These findings would tend to disprove the postulation that lanthionine formation is the cause of immunization.

The colorimetric procedure for lanthionine was not found acceptable for measuring lanthionine.

A postulated unhairing mechanism is given which would account for immunization, and is not dependent upon the rupture of disulfide linkages.

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BOOK NOTICE

Detergency Evaluation and Testing. By Jay C. Harris. Interscience Publishers Inc., New York, 210 pages, cloth, $3.75. The book is divided into nine sections as follows: Introduction, Screening Tests, Cotton Washing, Cotton Wash Test Methods, Wool Washing, Washing Procedures for Other Fibers, Hard Surface Cleaning, Radioisotopic Tracer Method and Miscellaneous Tests. Of particular interest to the leather chemist is Section II, Screening Tests. Here are given methods for determining acid and alkali stability, alkali solubility, stability toward metallic ions, surface and interfacial tension values together with spreading coefficient, lime soap dispersion, practical wetting tests, lather values and solubility in organic solvents. While the remainder of the book is largely devoted to textile procedures, there is much information of general value. Practically all examples of surface active agents are Monsanto products. The value of the book would be somewhat enhanced if other trade name products had been included. However the examples given are quite typical and their chemical formulae are given for comparison and guidance. Since the exceedingly rapid development in this field has flooded the chemists with hundreds of these compounds from which to choose, with the claims of the producers tending to emphasize the resulting confusion, any work giving simple, workable directions for testing the qualities desired is of real value. This book meets this requirement.

ABSTRACTS

The Physical and Mechanical Properties of Sole Leather and Their Determination. P. Chambard. *Bull. Assoc. Franc. Chimistes Inds. Cuir* **14**, 91 (1952). This is a lecture, decrying the inroads of substitutes in the sole leather field. One counter-measure is to improve quality, which is determined by the joint effect of numerous qualities. Wear

resistance, as determined by abrasion machines, does not correlate well with practical wear tests. Resistance to abrasion by sand blast may give more significant results. In any case leather soles probably cannot equal the substitutes in wear resistance. However, leather soles surpass substitutes in many properties affecting the wearer's comfort, and these properties ought to be further enhanced. Such properties included resistance to compression, and permeability to air and water vapor. Impermeability to liquid water, and resistance to water absorption should be improved. Method of manufacture and quality are discussed. The author believes that the old, slow tannage results in highest quality, but soles thus tanned will be a luxury item. Analysis is no longer capable of distinguishing leathers of slow and rapid tannage, but analyses are valuable in detecting loading materials. Loading with vegetable abstract is advantageous both to the seller and the consumer, as it results in a thicker sole from a hide of a given thickness, but loading with lignosulfonate, glucose, molasses, or $BaSO_4$ is condemned. Use of Epsom salt, to a strictly limited extent, is approved, as is use of light minerals such as talc or kaolin. H. B. M.

The Different Methods of Determining Water in the Analysis of Fatty Materials Used in Tanneries. J. Porte. *Bull. Assoc. Franc. Chemistes Inds. Cuir.* **14,** 130 (1952). The various possible methods (about 15) are listed (56 references). The widely used Dean-Stark method gives erroneous results if the fatty mixture contains methyl or ethyl alcohol, since the alcohol distils with the H_2O, and increases the volume of the aqueous phase. If the percentage of alcohol is known, a correction curve can be used; otherwise a chemical method must be employed, e.g., the CaC_2 method. H. B. M.

Determination of the Isoelectric Point of Collagen by Measuring the Difference of Membrane Potentials. Albert Staib. *Bull. Assoc. Franc. Chimistes Inds. Cuir,* **14,** 122 (1952); **15,** 17 (1953). The isoelectric point of a protein varies with experimental conditions and should always be stated with respect to the composition of the medium. Methods for determining I.E.P. are reviewed. The author used a modification of Loeb's method, based on the principle that, at the I.E.P., the pH of a gel is the same as that of the external solution in equilibrium therewith. The electrical system was: Sb-collagen strip-saturated KCl-external solution-Sb. The 2 electrodes were connected to a millivoltmeter, which showed no deflection when the pH values of the collagen and the external solution were the same. Collagen was prepared by liming goatskin with $Ca(OH)_2$, bating with pancreatin and NH_4Cl, treatment with a buffer solution at pH = 4.8, and extraction with 10% NaCl solution at pH = 7 to remove foreign proteins. Tests showed that removal of such proteins is most complete at pH values from 6 to 9, as shown by testing the extract with Almen's reagent. 4 g. pure tannin in 190 ml. 45° alcohol plus 2 ml. glacial acetic acid). Extraction was repeated until the extract gave a minimum precipitation with the reagent. The collagen was next treated with an acetate buffer at pH = 5, washed, electrodialyzed for 6 hours, and dehydrated with alcohol and acetone. The product contained 0.22% ash. Strips of this collagen were equilibrated with water containing variable amounts of 0.2*N* H_2SO_4 or NaOH. Each strip was pierced parallel to the grain and slipped over one Sb electrode. The strip dipped into saturated KCl, communicating through a capillary with the external solution (with which the collagen was equilibrated), into which the second Sb electrode dipped. No deflection of the millivoltmeter occurred for pH values (external solution) from 5.55 to 7.0. This is the isoelectric range of collagen in H_2O. When deflection occurred, the pH value of the collagen gel was determined by titrating the external solution to the point of zero deflection and measuring its pH vlaue. When the determinations were repeated in NaCl (0.1 *N* to *N*), the isoelectric ranges were different, and in some cases 2 isoelectric ranges were found, as follows: 0.1*N* NaCl, 5.10 to 7.00

and 8.6 to 9.65; 0.2*N*, 4.30 to 5.85 and 7.00 to 7.80; 0.5*N*, 3.85 to 5.30; *N*, 4.40-4.50. In some cases, notably the last, the experimental equilibrium pH values are so widely spaced that the limits of the isoelectric zone may be at least 0.5 pH units above and below the figures given. H. B. M.

Removal of Stoppers from Tubing. By R. Huber. *Chemist-Analyst* **42,** 72 (1953). Tight fitting rubber stoppers can often be removed safely from glass tubing by use of a second rubber stopper. This second stopper, preferably of larger size, is partially inserted on a straight end of the tubing. Careful twisting of the second stopper, while holding the frozen stopper stationary, will usually loosen the latter.

Preparation of Stable Starch Indicator. By W. D. Nordling. *Chemist-Analyst* **42,** 70 (1953). The following starch solution showed no sign of deterioration after at least 6 months. Add 50 ml. of glycerin and 50 ml. of distilled water and bring to a boil. Add a mixture of 1.0 g. of soluble starch with 2-3 ml. of water, stir and continue boiling for 3 minutes. Cool to room temperature and use or store.

Oxidimetric Determination of Tannins. By V. Kubelka and B. Glozic. *Tech. Hlidka Kozeluska* **24,** 10, 51, 78 (1949). Through *C.A.* **47,** 9648 (1953). Factors influencing the $KMnO_4$ titration of tannins followed by iodometric back-titration were studied. $KMnO_4$ consumption increased with concentration, with time of contact with $KMnO_4$ before back titration (10 minutes was recommended), and with heating time (oxidation was not complete even after boiling for one hour), with room temperature, and with amount of H_2SO_4, slightly with amount of tannin present, with excess of $KMnO_4$ added, and with time of standing of the tannin solution in air. Agitation had no effect. The iodine liberated prior to back-titration combined with tannins, but less so with the partly oxidized tannins after addition of excess $KMnO_4$; with the latter the reaction was slow enough so that immediate titration with $Na_2S_2O_3$ avoided any error. A correction for the effect of oxidizable soluble compounds from the hide powder was necessary. A comparison of the original Loewenthal method and four proposed modifications showed that, while all were applicable to natural tannins, for synthetic tannins and their mixtures with natural tannins only those methods were applicable which were standardized by comparison with the same mixtures. Also, the methods were not applicable for used tannery solutions, because hide combines first with the more difficulty oxidizable compounds in tanning solutions, thus changing the standardization factor.

Polarographic Studies in Leather Chemistry. IV. By A. K. Vlcek, E. Spalek and L. Kratky. *Tech. Hlidka Kozeluzska* **24,** 65 (1949). Through *C.A.* **47,** 9650 (1953). The polarography of ninhydrin was studied at 20° in concentrations of 10^{-4} to 10^{-5} *M* in the presence of 0.4 *M* Na_2SO_4 and Britton (B) or Sorsensen (S) buffers. In B. buffers 3 waves can appear, in S. buffers 5, and their presence, half-wave potential, and height depended on the pH. To explain this, an equilibrium between 4 forms of ninhydrin, of different degrees of hydration of the CO groups, was postulated, only the nonhydrated groups being reducible. The H_3BO_3 present in B. buffers also formed complex anions with 2 of the forms. The theory was confirmed by calculating the change in height of one of the waves with pH and H_3BO_3 concentration and obtaining good agreement with experimental data. For the polarographic determination of ninhydrin, use of solutions containing Na_2SO_4 and $Na_2B_4O_7$ was recommended; only one wave, with height proportional to concentration, was then obtained.

Fixation of Vegetable and Synthetic Tannins. By K. Ullrich. *Tech. Hlidka Kozeluzska* **24,** 48 (1949). Through *C.A.* **47,** 9650 (1953). Two fixation agents were tested and found to achieve better utilization of tanning agents. Eskafix OB is based on degraded proteins, Eskafix AK is a polymer of low molecular weight with C and N alternating in the chain and O-containing side chains.

Chemical Analysis of Chrome Tanned Leather. II. Critical Experiments on the Chromic Oxide Content and Tanning Degree in Chrome Tanned Leather. By V. Kubelka. *Tech. Hlidka Kozeluzska* **24,** 75 (1949). Through *C.A.* **47,** 9651 (1953). In tanning experiments with hide powder and Cr sulfate solutions, it was found that increasing basicity increased the Cr_2O_3 content of the leather, whether the base was present in the original solution or added subsequently. Differences in the preparation of the Cr sulfate solution (chrome alum solution or reduction of $K_2Cr_2O_7$ with glucose in H_2SO_4 solution) had no effect. Aging of the solution slightly increased the Cr_2O_3 content of the leather. Pickling with acid decreased the Cr_2O_3 in a calculable manner. Subsequent neutralization increased it again, but the extent could not be calculated. The constant Cr content of leathers previously examined was due to similarity of treatment.

Synthetic Tannin SPS. By P. S. Konovalenko. *Legkaya Prom.* **12,** No. 2, 33 (1952). Through *C.A.* **47,** 10255 (1953). This syntan is based on technical polyphenols. It has high firming and filling characteristics. Analysis (shaking with hide powder for 10 minutes) gave 455.9 solubles, 5.4 insolubles, 208.2 nontannins and 247.7 tannin grams per liter. pH of solution was 3.9. For tanning soft leathers, SPS can be used alone; for tanning tough saddle leather, a mixture of 50 per cent SPS and 50 per cent vegetable tannin is recommended.

Characteristics of Tanning with Basic Chrome Salts in the Presence of Ammonium Sulfate Salts. By S. A. Kuraitis, I. A. Khokhlov, and A. M. Lyubimova. *Legkaya Prom.* **12,** No. 1, 28 (1952). Through *C.A.* **47,** 10257 (1953). Differences between the actual basicity of chrome liquor containing NH_4 sulfate salts and that determined by the standard Russian method are due to the fact that these salts are titrated with alkali, similarly to H_2SO_4. The following method of analysis is proposed: dilute the liquors to give 3.5 to 4.5 g./l of Cr_2O_3; dilute spent liquors to twice their volume. Add 5 ml. of 10 per cent Na_2CO_3 solution, dilute with water to 250-300 ml., add 4.5 g. $NaHCO_3$, distil, and determine NH_3 in the distillate. Determine Cr_2O_3 by the standard Russian method. To determine sulfuric anhydride, add to 5 ml. of chrome liquor 0.1 *N* KOH equivalent to the 0.1 *N* acid consumed in determining NH_3, add 0.2 ml. phenolphthalein, boil until free of NH_3, and then titrate to permanent light pink.

Tanning of Heat-Stable Youfts. By M. S. Qvrutskii and S. Chaikovskii. *Legkaya Prom.* **12,** No. 5, 23 (1952). Through *C.A.* **47,** 10257 (1953). By using one mole of formic acid per mole of Cr_2O_3 in the pickle, with subsequent retanning in one phase with oak extract, the liquid coefficient being 12 and the initial pH of liquors 5.5, the washing out of chrome is practically eliminated.

Tanning Extract from Eucalyptus Bark. By M. N. Krasukhhin. *Legkaya Prom.* **12,** No. 7, 20 (1952). Through *C.A.* **47,** 10257 (1953). In mixtures with oak extract, (1:1 on tanin basis), eucalyptus bark extract is suitable for tanning sole leather.

Distribution of Ions Between Hide Substance and the Surrounding Liquid During Acid Swelling. By O. V. Matveeva and A. N. Mikhailov. *Legkaya Prom.* **12,** No. 8, 18 (1952). Through *C.A.* **47,** 10257 (1953). The equilibrium of collagen with HCl and H_2SO_4 is approximately in accord with the Donnan equilibrium only in pH zones sufficiently far from the isoelectric point of the protein. In zones close to the isoelectric point of collagen, the equilibrium follows more complex relations; the Donnan theory cannot be used for calculating this equilibrium.

Resin Tannage. I. Tanning with Dimethylolurea. By Y. Hachihama and Y. Kyogoku. *J. Chem. Soc. Japan* **55,** 129 (1952). Through *C.A.* **47,** 10257 (1953). In order to examine the usability of dimethylolurea as a tanning agent, its reaction with gelatin, and its absorption by hide have been studied. The possibility of tanning with dimethylolurea is suggested.

Tests and Specifications for Synthetic Tannins. V. The Dependence of the Results of the Quantitative Determination of Synthetic Tannins on the Sample Weight. By E. Kubeckova. *Tech. Hlidka Kozeluzska* **24,** 217 (1949). Through *C.A.* **47,** 10257 (1952). In testing the results of synthetic tannin determination for independence of sample weight, amounts varying from A/8 to 2A are now used, where A is the weight used for the usual analytical solution. It is shown that the lower weights give too low precision, and amounts of 0.5A, 3/4A, A, 1.5A and 2A are recommended.

Tests and Specifications for Synthetic Tannins. VI. By V. Kubelka and E. Kubeckova. *Tech. Hlidka Kozeluzska* **24,** 302 (1949). Through *C.A.* **47,** 10257 (1953). The present laboratory scale evaluation of synthetic tannins by tanning for 14 days with shaking is not sufficient. A method of tanning at rest for 6 weeks was tested with 7 synthetic tannins, alone and in 1:1 mixtures with natural tannins. The density, composition, and pH of the tanning liquors were determined at intervals during tanning, and the finished leather examined and analyzed. The concentration of the tanning liquor was gradually increased during the first 4 weeks of tanning from 7 to 60°E. The tanning method is described in detail.

Studies of Tannery Effluents. III. Effluents of a Glue and Gelatin Factory. By A. Bycichin, C. Halamek, and K. Hlavacek. *Tech. Hlidka Kozeluzska* **24,** 321 (1949). Through *CA.* **47,** 10257 (1953). A summary of the amount, composition and treatment of glue and gelatin wastes in Gottwaldov.

Semiworks Testing of Synthetic Tannins for Official Recognition. By I. Binko and K. Müller. *Tech. Hlidka Kozeluzska* **24,** 366 (1949). Through *C.A.* **47,** 10257 (1953). Detailed plant procedure for the plant testing of new synthetic tannins is described.

Tannin Fixation Value of Natural Tanning Agents. Its Significance and Determination. By E. Kubeckova, L. Pospisil, and M. Pokorny. *Tech. Hlidka Kozeluzska* **24,** 354 (1949). Through *C.A.* **47,** 10257 (1953). The Stather-Herfeld method for the determination of tannin fixation values by weighing the hide powder before and after treatment with tanning agent and washing, and the authors' modifications (different washing procedure and nitrogen determination in the tanned hide powder) were applied to 14 natural tanning agents. On the basis of the comparison, a new method is described in detail.

Graphical Calculation of Chrome Tanning Liquors for Single Bath Tanning. By B. Köhler. *Tech. Hlidka Kozeluzska* **24,** 129 (1949). Through *C.A.* **47,** 10258 (1953). Diagrams are given for the evaluation of the amounts of substances required for the preparation of chrome tanning liquors of a desired basicity, and the amounts of neutral salts produced as by-products.

Analysis of Vegetable Tannins in the Year 1948. By L. Masner. *Tech. Hlidka* Kozeluzska **24,** 202 (1949). Through *C.A.* **47,** 10258 (1953). Analytical results of vegetable tannins and dyewood extracts are given.

Sulfonated Novolaks as Synthetic Tannins. II. By I. Binko and J. Kolav. *Tech. Hlidka Kozeluzska* **24,** 225 (1949). Through *C.A.* **47,** 10258 (1953). Sulfonated novolaks prepared in the ratio of 0.75 to 0.85 mole CH_2O and 0.15 to 0.25 mole H_2SO_4 to one mole phenol are good tanning agents, giving leather with 90-120 degrees of tannage. The optimum ratio is 0.85 CH_2O: 0.25 H_2SO_4: 1 PhOH. Plant tests with these and more strongly sulfonated novolacs in 1:1 mixture with vegetable tannins showed good pH control of tanning liquors, small turbidity, and rapid tanning. The slicked cow leather product was within specifications, except for high water absorptions.

The Possibilities of the Cultivation of Tannin Bearing Plants in Czechoslovakia from the Botanical Point of View. By J. Kahelik. *Tech. Hlidka Kozeluzska* **24,** 136 (1949). Through *C.A.* **47,** 10258 (1953). The possibility of growing edible chestnuts and other domestic, tropical, and subtropical plants containing tannins in roots or leaves is discussed. Their tannin content and its variation with the seasons is given. Since fresh bark yields more tannins than dry bark, extraction in the forest is recommended. For analytical determination of tannins, extraction with 40 per cent acetone is preferable to water extraction.

Polarographic Studies in Leather Chemistry. V. Polarograms of Aqueous Solutions of Degradation Products of Tanning Agents: Gallic Acid, Protocatechuic Acid. By A. K. Ulcek, E. Spalek, and L. Kratky. *Tech. Hlidka Kozeluzska* **24,** 258 (1949). Through *C.A.* **47,** 10258 (1953). If special precautions are taken against air oxidation, no cathodic waves are observed, contrary to observations of Browning. Both gallic and protocatechuic acids show 2 anodic waves. The larger is a diffusion wave. Its half-wave potential decreases with increasing pH and its height is proportional to the concentration. The smaller is an adsorption wave. Its half-wave potential decreases with increasing pH, and its height is given by Langmuir's adsorption isotherm and varies linearly with the height of the mercury column. The oxidation of the two mentioned acids probably leads to quinone-like intermediates, and the smaller waves are due to the adsorption of the latter. The half-way potentials of tannin degradation products decrease in the order: protocatechuic acid, pyrocatechol, gallic acid, hydroquinone, pyrogallol. Resorcinol and phloroglucinol give no waves. Each compound can be determined in pure solution, but not in mixtures.

Evaporation in Thin Layers. By Z. Renelt. *Tech. Hlidka Kozeluzska* **24,** 155 (1949). Through *C.A.* **47,** 10259 (1953). An evaporator for tanning liquor is described. Its advantages are short heating time, continuous operation, possibility of evaporating to any desired degree, small need of supervision, no encrustation on the evaporating surface, easy cleaning, and small space requirement.

Colorimetric Determination of Phosphates in Egg Yolks and Water Used in Tanneries. By I. V. Kubelka and Z. Novak. *Tech. Hlidka Kozeluzska* **25,** 41 (1950). Through *C.A.* **47,** 10259 (1953). The molybdenum blue method for P determination, with $SnCl_2$ as a reducing agent, was studied. The NH_4 molybdate -H_2SO_4 solution should be added first, then the $SnCl_2$ solution pipetted under the surface to prevent turbidity. Colors were read 3.5 - 7 minutes after development. Higher temperatures, up to 50°, hindered color development. The amount of the NH_3 molybdate solution added or the total volume of solution used had no effect. The pH should be below 1, but excess free acids should be neutralized.

Production Control in Tanning Extract Manufacture. By L. Masner. *Tech. Hlidka Kozeluzska* **24,** 303 (1949). Through *C.A.* **47,** 10259 (1953). A new method is given of sampling spent tan from the extraction of vegetable tanning agents, along with a particle size determination of by sieving. In calculating the extraction yield, a correction for the apparent formation of tannin during the drying of the spent tan must be made separately for each kind of tanning material. The method gives results concordant with those obtained by a more tedious material balance.

The Mechanical Testing of Leather. III. Further Experiments in the Determination of Water Permeability of Leather. By V. Kubelka and Z. Novak. *Tech. Hlidka Kozeluzska* **24,** 113 (1949). Through *C.A.* **47,** 10259 (1953). Water permeability co-efficients of leather soaked in water for 7 days, dried for 48 hours, and kept at 60-65 per cent relative humidity for 24 hours were lower than those of the original leather, and the results were more reproducible. The effect of compression was entirely eliminated by soaking.

The Mechanical Testing of Leather. IV. Attempted Determination of Leather Stiffness by Measurement of Compressibility. By V. Kubelka and J. Ott. *Tech. Hlidka Kozeluzska* **24,** 203 (1949). Through *C.A.* **47,** 10259 (1953). The compressibility of 94 samples of sole leather samples was measured in a previously described apparatus. Each sample was measured dry, after soaking 24 hours, and after air drying for 48 hours at 22°. On the basis of these results, specifications for pit and drum tanned butts, shoulders, and bellies are suggested.

Mechanical Testing of Leather. V. Determination of Leather Stiffness by Bending Measurements. By L. Kubelka and J. Vleck. *Tech. Hlidka Kozeluzska* **24,** 209 (1953). Through *C.A.* **47,** 10260 (1953). An apparatus was designed for measuring either the bending angle of a leather strip at constant load, or the load required for bending through a given angle. The first method gave results depending on the load, because of variation in the effective sample length. The second method required continuous additions of weights, which was achieved by slow additions of Hg to a tared beaker. The results correlated well with stiffness determinations by the compressibility method, showing that the same physical property was being measured. An improvement in the apparatus will be attempted.

A Proposal of Uniform Analytical Methods for Leather Fats and Greases. By M. Spicka. *Tech. Hlidka Kozeluzska* **24,** 280 (1949). Through *C.A.* **47,** 10259 (1953). Methods for the determination of chemical composition and physical properties of leather fats and greases, mineral oil, soap, egg yolks, degras, and sulfonated fats are proposed.

Application of Chloroprene Latex to the Finishing of Leather. By I. Binko. *Tech. Hlidka Kozeluzska* **24,** 289 (1949). Through *C.A.* **47,** 10260 (1953). The use of chloroprene latex in casein paints for leather, instead of synthetic resins, is recommended. High temperature drying vulcanizes the latex and coats each pigment particle with rubber. Vegetable tanned leather must be dried at lower temperatures than chrome tanned leather, but the tannins act as vulcanization accelerators. The products have good water and wear resistance.

New Deliming, Tanning, and Finishing Products. By B. Kohler. *Tech. Hlidka Kozeluzska* **24,** 361 (1949). Through *C.A.* **47,** 10260 (1953). The application of new products made from oil refinery wastes to the deliming of hides, pretanning of light leather, and leather currying and finishing is described.

Fatliquoring of Chrome Leather. By I. I. Khokhlov. *Legkaya Prom.* **12,** No. 4, 19 (1952). Through *C.A.* **47,** 10260 (1953). The iodine number of fish oil suitable for fatliquoring chrome leather should not exceed 100-110.

Photocolorimetric Determination of Chrome Oxide in Fur Skins. By N. M. Rybovalova. *Legkaya Prom.* **12,** No. 4, 24 (1952). Through *C.A.* **47,** 10260 (1953). The existing method is improved by adding untanned hydrolyzed skin to the standard solution. Results are in agreement with results obtained by standard mthod of fusing with oxidizing mixture.

A Study of the Fatliquoring of Leather. By H. T. Arend. *Tech. Hlidka Kozeluzska* **24,** 229 (1949). Through *C.A.* **47,** 10260 (1953). A review of the theoretical aspects of fat absorption by leather from emulsions, including the functions and composition of the emulsion components and the factors influencing absorption.

Chrome Leather from Seal Skins. By M. Y. Kutovskii. *Legkaya Prom.* **12,** No. 2, 28 (1952). Through *C.A.* **47,** 10260 (1953). Chrome tanned leather was satisfactory except for fat content (up to 13.6 per cent) and natural creases. Retention of fatliquoring in process is to be investigated.

Cleavage of Collagen. By I. S. Shestakova. *Legkaya Prom.* **12,** No. 2, 30 (1952). Through *C.A.* **47,** 10260 (1953). Cleavage of collagen is the aggregate of processes of separation into its structural elements, accompanied by the destruction of different forms and types of bonds and the formation of new bonds in products formed during the change in the collagen.

Accelerated Determination of Alumina in Leather. II. Attempted Polarographic Determination of Aluminum. By V. Kubelka and J. Hradsky. *Tech. Hlidka Kozeluzska* **24,** 107 (1949). Through *C.A.* **47,** 10260 (1953). The direct polarographic determination of aluminum in solutions, obtained by wet combustion of leather was impossible because of interference by other solution ingredients. The possibility of amperometric titration with 8-quinolinol is discussed. An indirect amperometric titration, depending on precipitation of aluminum with $(NH_4)_2HPO_4$, filtration, dissolving the precipitate in hot 10 per cent HNO_3, and amperometric titration with $BiOClO_4$ to precipitate $BiPO_4$, was studied and

found promising; if the $AlPO_4$ solution is titrated into $BiOClO_4$ solution. This method is somewhat more rapid than the gravimetric, but the results are slightly low.

Parkia Filicoidea Pods from Nigeria. By R. W. Pearman. *Colonial Plant and Animal Products* **3,** 231 (1953). The pods are from 9 to 12 inches in length, with pod cases constituting 36 per cent of the total weight. The cases contain 22 per cent tannin. Extract made from the liquor would show rather low purity. The tan liquors have a tendency to develop mold readily and become slimy during use. Although the leather forming properties of the tannin extracts are promising, the drawbacks previously mentioned can well overcome the good qualities. It is suggsted that bisulfiting might prove beneficial.

Mopani Bark from the Beehuanaland Protectorate. By H. Bennett and R. W. Pearman. *Colonial Plant and Animal Products* **3,** 232 (1953). Bark from *C.mopani* showed only 5.9 per cent tannin and although sheepskin tanned in the infusion was satisfactory, an extract of the material would be impractical because of its low purity.

Spent Mangrove Bark from North Borneo. By H. Bennett and R. W. Pearman. *Colonial Plant and Animal Products* **3,** 234 (1953). Since spent mangrove bark contains 10.4 per cent ash on the dry basis, analyzing 70 per cent $CaCO_3$, it is suggested that the ash can be used as a soil conditioner.

The Caesalpinias as Tanning Materials. By F. N. Howes. *Material Vegetabiles* **1,** 60 (1953). Through *Colonial Plant and Animal Products* **3,** 253 (1953). The author has collected together much information concerning a number of species of the *Caesalpinias,* including countries of growth, botanical data of the plant or shrub, details of planting and growth, description of the portion used for preparation of tanning material, its tannin content and type of leather obtained. The most important species known to the trade are (a) *Caesalpinia coriaria* Willd or divi divi or libi dibi, (b) *Clbrevifolia* Bail or argarobilla, (c) *C.spinosa* Mol. or tara, and (d) *C.digna Rotte,* or Tari or teri.

Eucalypts as Tanning Materials. By R. W. Pearman. *Colonial Plant and Animal Products* **3,** 206 (1953). About 500 species of eucalyptus trees, indigenous to Australia, are known, but only a few are of commercial importance. About 1,450 tons of bark of *E.astringens* Maiden, or "Brown Mallet", containing 40 - 57 per cent tannin, are produced annually for export, most of it going to Europe. A small amount is used in Australia for blending with wattle bark and other tanning materials. In the early thirties mallet bark of commerce consisted of a mixture of *E.astringens, E.gardnerii* Maiden, "Blue Mallet", and *E.falcata* Turcz., "White Mallet", giving an average tannin content of 40 per cent. Only the Brown Mallet is employed now. In 1935 the production of a tannin extract from "Wandoo" was started. Two species are used, namely: *E.reducta* Schauer, *var.elata Beuth.,* "Wandoo", and *E.acedens* W. V. Fitzgerald, "Powder Bark Wandoo". The whole tree, except foliage, is used. About 65,000 tons Wandoo are used annually for the production of extract, marketed under the name Myrtan. About 25 per cent of the extract is used in Australia, while the remainder is exported. The trees attain a height of 50-60 feet, and an average girth of 6 feet. The wood shows 7.8 and the bark 16.7 per cent tannin respectively. The extract is a mixture of catechol and pyrogallol tannins. It produces a leather somewhat pink in color, which darkens readily on exposure to light. It penetrates pelt more quickly than chestnut and gives a firm, solid leather. Although the cultivation of euclayp-

tus in Morocco, Belgian Congo, Union of South Africa, Kenya and other colonies has not proved successful from the tannin recovery standpoint, nevertheless there are rather extensive plantations in the Union of South Africa and Kenya where the wood is used for railway fuel.

Warbled Hides in the United States. By K. Trcka. *Koza i Obuca* (Leather and Footwear) **2,** 175 (1953). The author describes the extent of the warble in the United States and steps taken to decrease its prevalency. He cautions the Jugoslavian hide buyer when entering the American market to note whether his hides are warble damaged.

How to Improve the Conservation of Pig Skins in Our Country. By Z. Bayer. *Koza i Obuca* (Leather & Footwear) **2,** 179 (1953). Experience with the use of salt with soda, naphthalene and Merpin S extra 40 added is described.

The Roles of the Amino and Hydroxyl Groups of Collagen in Its Reactions with Formaldehyde, Tannic Acid and Quinone. By R. W. Green. *J. Amer. Chem. Soc.* **75,** 2729 (1953). Hide powder was acetylated to give a series of collagen derivatives containing varying proportions of N- and O-acetyl groups. Two-gram samples of untreated and treated collagen were allowed to react in buffered solution with formaldehyde, quinone and tannic acid, respectively. Curves are shown wherein *m*moles total acetyl per gram of collagen are plotted against *m*moles tanning agent per gram of collagen. Both the quinone and formaldehyde curves show an abrupt drop in tannin fixation up to about 0.4 *m*moles acetyl per gram of collagen. The tannin curve shows no abrupt change. All show a gradual decline, beyond with increasing acetylation. Possible explanation of results is given.

The Adsorption of Water Vapor on Acetyl Derivatives of Collagen and Silk Fibroin. By R. W. Green and K. P. Ang. *J. Amer. Chem. Soc.* **75,** 2733 (1953). The adsorption of water vapor on acetyl derivatives of collagen and silk fibroin has been studied by the isopiestic method and the equation of Brunauer, Emmett and Teller used to analyze the adsorption isotherms. First layer adsorption is appreciably reduced by acetylation, but this is not a specific effect of the amino and hydroxyl groups, which retain their power to coordinate water. It is suggested that a proportion of the first layer water molecules are adsorbed on the polypeptide chain and that it is these molecules which are displaced in the rearrangements accompanying acetylation.

Helical Polypeptide Chain Configuration in Collagen. By C. Cohen and R. S. Bear. *J. Amer. Chem. Soc.* **75,** 2783 (1953). Application of methods for testing X-ray diffraction data for evidence of helical chain configuration shows that helical structures heretofore proposed do not account for the wide-angle diffractions of collagen. The authors propose a discontinuous helix with 2 turns and 7 roughly equivalent scattering groups per 20 Å. of axial projection which should contribute to near-meridianal diffraction according to Bessel functions of n order. The approximately seven-fold screw axis does not permit exact hexagonal packing of fibril chains, but no evidence shows this to be necessary. Density requires about 21 amino-acid residues along 20 Å. of helix axis. The 7 nearly equivalent groups should, therefore, comprise 3 residues each. The above analysis does not determine uniquely the chemical connection of the residues.

Application of Ion Exchange Chromatography to the Enzymatic Resolution of Amino Acids. By C. G. Baker and H. A. Sober. *J. Amer. Chem. Soc.* **75,** 4058 (1953). Conditions are described for the isolation of the optical isomers of nine representative racemic amino acids by the application of a cation exchange column separation to the products of an asymmetric enzymatic hydrolysis procedure. This separation procedure is conveniently applicable to the resolution of relatively small amounts of initial racemic substrates equivalent to 0.3 to 1.0 g. of the amino acid enantiomorph.

The Surface Areas of Proteins. VI. Vapor Phase Titrations with Polar Gases. By S. W. Benson and J. M. Seehof. *J. Amer. Chem. Soc.* **75,** 3925 (1953). The irreversible sorption of HCl, BF_3, CH_3NH_2 and NH_3 on a series of representative proteins has been investigated with the intention of determining the chemical reactivity of the protein as a function of the aforementioned gases. Methods have been developed which distinguish between "free" basic and "free" amino groups and which show promise of being able to elucidate the internal structural features of many proteins and indeed of other large organic molecules. It has been found possible to titrate the free amino groups by two independent methods and the free basic groups by another, the agreement of the free amino groups with chemical analysis being marked. The whole procedure is carried out in a vacuum system and at no time do the proteins come into contact with anything except the reacting gas, water vapor and all solvents being excluded from the process. It is proposed that the irreversible sorption of polar gases is merely the end point of the more general hysteresis phenomenon and that hysteresis itself can be considered as being intimately tied up with the chemical groupings within a protein.

A Model for the Configuration of Sulfhydryl Groups in Proteins. By R. E. Benesch and R. Benesch. *J. Amer. Chem. Soc.* **75,** 4367 (1953). Because of the speculation concerning the differing reactivity of protein -SH groups and, especially, the marked increase in their reactivity upon denaturation of the protein, the authors report two sets of observations from which they devise a compromise between chemical and physical theories. These theories were proposed to account for the masking of protein -SH groups, since it is postulated that a chemical link (hydrogen bonding) leads to steric hindrance by branched aliphatic side chains.

The Adulteration of Industrial Salt for Salting Hides. By E. Simoncini. *Cuoio, Pelli. Mat. Concianti* **29,** 5 (1953). Through *C.A.* **47,** 9039 (1953). Microorganisms, including molds, originally found in raw hides, were cultured on gelatin or agar containing industrial salt, alone or with various additives. The best results, indicated by minimum growth of microorganisms and best preservation of hide after one month, were obtained with salt containing: (a) 3.5 per cent Na_2CO_3 plus 1 per cent naphthaline; (b) 1 per cent alum plus 2 per cent naphthalene; (c) 2 per cent Merpin W S extra 40. Spots on the hides were very scarce with salt containing: (d) 2 per cent Na_2CO_3 plus 0.4 per cent petroleum; (e) 5 per cent of 10° Bé sodium hypochlorite plus 0.25 per cent alum; (f) 5 per cent alum plus 0.005 per cent Orange II; (g) 0.05 per cent Na_2S plus 0.01 per cent Sulfur Blue.

Hydrothermal Stability and Intramolecular Organization of Collagens from Mammalian and Teleost Skins. By K. H. Gustavson. *Svensk. Kem. Tidskr.* **65,** 70 (1953). Through *C.A.* **47,** 9039 (1953). Collagen from the skins of mammals show greater hydrothermal stability than those of teleosts, as measured by the temperature Ts

at which instaneous shrinkage of the collagen fibers occurs. Ts is 60-70° for mammals, about 40° for salt water teleosts, and about 55° for fresh water teleosts. It is suggested that the lower Ts for teleosts is due to their lower hydroxyproline content, since the OH groups of the latter are believed to play an important part in collagen stabilization.

Rapid Tanning with Sound Waves. By E. Simoncini and I. Criscuolo. *Cuoio, Pelli Mat. Concianti* **29,** 82 (1953). Through *C.A.* **47,** 9039 (1953). Experiments of tanning hides with the aid of low-frequency sonic waves (50 Hz) obtained with a magnetic vibrator, show that the vegetable tanning baths are exhausted without alteration of the tannin-non-tannin ratio, but the amount of tannin combined in unit time increases, compared with the untreated samples.

A New Tanning Agent—Furfuryl Alcohol. By I. Brihta, A. Glavas and J. Dugosevic. *Kemija u Industriji* (Zagreb) **2,** 145 (1953). Through *C.A.* **47,** 9039 (1953). A good tanning effect was achieved by impregnating hides with furfuryl alcohol, which was subsequently submitted to a condensation process by immersing the impregnated hides in a solution of a mineral or a stronger organic acid such as lignosulfonic acid. According to the strength of the condensing acid solution, softer and lighter, or harder and darker leathers were obtained. No deterioration of the leather was noted within one year after tanning. A tanning effect was also produced by merely exposing to the air, hides impregnated with furfuryl alcohol.

The Celebration of a Centenary. By A. Simoncini. *Cuoio, Pelli, Mat. Concianti* **29,** 134 (1953). Through *C.A.* **47,** 9040 (1953). A lecture on the first patent on tanning with chrome salts by Hylten Cavalin (1853).

Dyeing of Glove Leathers. By A. Simoncini. *Cuoio, Pelli, Mat. Concianti* **29,** 92 (1953). Through *C.A.* **47,** 9040 (1953). The skins should be degreased with ammonia and a nonionic detergent.

Viscosity and Structure of Vegetable Tannins. By A. Basinski, M. Czerniawski, and J. Skraga. *Prace Glownego Inst. Chem. Przemysl* (Poland). No. **3,** 40 (1951). Through *C.A.* **47,** 9647 (1953). The viscosity of extracts of chestnut, quebracho "Korona", oak, and ordinary quebracho were studied. Viscosity increased linearly with concentration, decreased with increased temperature, and did not obey Einstein's law. Under identical conditions these extracts showed definite differences in viscosity at the same concentration and from the viscosity measurements the percentage of tannin in the extracts could be calculated. Chestnut and "Korona" quebracho showed increased hydration with increased concentration, while oak and ordinary quebracho showed an insignificant increase.

Polyvinyl Alcohols in Leather Processing. By T. A. Dickinson. *Leather and Shoes,* **126,** No. 22, 10 (1953). It would seem that polyvinyl alcohol resins should find considerable use in leather manufacture. They are not expensive. They are completely soluble in water and yet may be insolubilized by such agents as cupric chromate, sodium dichromate

and chromic nitrate. Plasticized and unplastized these resins have been used with considerable success, dispersed in water along with insolublizers, as leather impregnants, imparting body and reducing the softening effects of oils. When materials require a maximum resistance to oils and grease, polyvinyl alcohols alone are excellent finishing media because completely impervious to vegetable, animal and mineral lubricants. R. H. T.

Water Repellent Dyes for Leather. By R. Hauck and R. M. Lollar. *Leather and Shoes*, **126,** No. 22, 11 (1953). The recently described synthesis of regular acid and basic dyes with a long hydrophobic side chain would seem to have interest to the leather manufacturer. For a study, such dyes were synthesized (diazotized para-rosanaline derivatives) and their dyeing qualities compared with standard dyes and also with dyes of similar constitution prepared by Dr. DeWitt of Michigan State College. The long tailed dyes gave the leather some water repellency. None were especially washable with soap. The colors do not fade appreciably, which is very desirable. Some of the leathers showed very favorable low bleeding onto a moist cloth, and very little wet or dry crocking. The results indicate possible valuable developments in this field. R. H. T.

Water Repellency of Leather. By W. T. Roddy. *Shoe and Leather Reporter*, **272,** No. 8, 25 (1953). While fatliquored leathers have some water repellency and stuffed leathers have considerably more, it has not been found possible, by such means, to make leather lastingly water repellent under wearing conditions. Actually 15-30 minutes is about as long as water is repelled. Even with such a short time the water vapor permeability is considerably reduced. Consequently efforts have been made to accomplish water repellency in other ways. The use of high polymers has shown some promise. The same is true for water repellent dyes. It has been found that silicones, properly applied, will give long time water repellency without seriously reducing water vapor permeability. A product of unknown composition, because of the patent situation, under development at the Moench Tanning Co., appears to accomplish a like result. The problem of the best point of application is still to be solved. R. H. T.

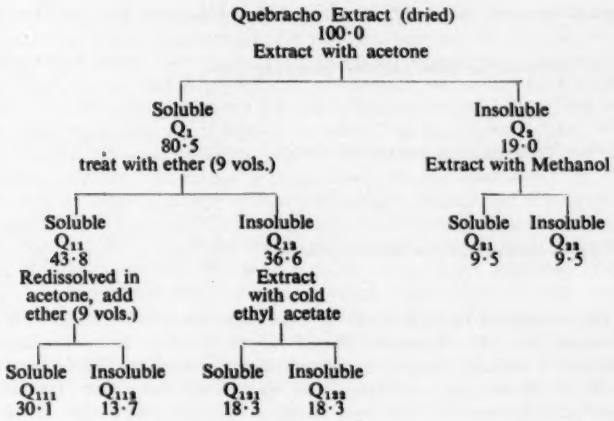
Loose Grain as a Consequence of Hydrolysis. By P. Bocciardo. *Cuoio-Pelli-Materie Concianti*, **29,** No. 5 (1953). The author believes that the primary cause of loose grain may be found in conditions which prevail in the hide preliminary to tanning. The hide is composed of five layers, the epidermis, the papillary layer (grain), the subpapillary layer, the reticular layer and the deep layer. As the epidermis is removed with the hair, the tanner is concerned with the next layer, the papillary layer, when considering loose grain. The sub-papillary layer is the seat of the sebaceous glands and the thermo-regulator agents, which render it the most delicate and the most easily affected by hydrolysis. This layer, before salting or as the result of faulty salting, may be considerably attacked by bacteria, producing a hydrolysis which may be manifested in falling hair and in loose grain after tannage. This zone is also most accessible to chemicals (by way of the hair follicles) as well as to bacteria. Hence excessive chemical treatment during depliation may also bring about hydrolysis, later resulting in loose grain. R. H. T.

Note on the Mechanism of Vegetable Tannage. By S. G. Shuttleworth. *J. Soc. Leather Trades' Chemists*, **37,** 258 (1953). This is a comment on the following statements from a recent article published in the *J. Soc. Leather Trades' Chemists*, **37,** 206 (1953).

"In vegetable tanning, tannin first combines with the basic groups of collagen and probably links them by hydrogen bonds to the peptide groups. It is the tannin attached to the arginine groups which raise the shrinkage temperature of the hide." Reasons are given for considering these statements unsound. R. H. T.

The Average Molecular Weight of Black Wattle and Other Condensed Tannins. A Critical Review of Materials and Methods. By D. G. Roux. *J. Soc. Leather Trades' Chemists*, **37**, 259 (1953). In the past molecular weight investigations have been handicapped by three complications. (a) The complete elimination of carbohydrate non-tans could not be accomplished without altering the nature of the tannin. (b) No suitable method was available for covering the molecular weight range from 500 to 2000. (c) Suitable solvents had not been used. Deviations from Raoult's law occur frequently and cause anomalous values in molecular weight determinations. Examples are given of such false values obtained in cryoscopic studies of molecular weights of polypeptides of known molecular weight. Referring to the solvents, non-polar bromoform gave correct values for all the molecules tested; but highly polar acetic acid gave accurate values for only a few. Previous work on black wattle tannin is summarized in a table which shows molecular weights varying from 432 to 1760. The highest values were obtained with tannins purified by electrodialysis which, by its nature, is bound to result in high molecular size. Cryoscopic determinations of the derivatives of black wattle tannin in dioxane run from 1700 to 3000 average molecular weight. Dioxane is an unsuitable solvent for such determinations. All previous work on the 95 per cent tannin extract of black wattle extract fraction separable by electrodialysis indicates a molecular weight in the neighborhood of 1700. Neither this nor the value around 550 for the crude extract of 70 per cent tannin content is correct. The present investigation is an attempt to clarify some of the confusion. The tannins were obtained from commercial extract. They were isolated from sugars by lead-salt precipitation, and from gums by repeated extraction with methyl alcohol. The purified product was methylated with dimethyl sulfate and alcoholic KOH in the usual way, and finally subjected to chromatography in an alumina column to remove incompletely substituted material. The product (36.5 per cent methoxyl) was pale yellow in color. Cryoscopic determinations, using benzene, as a solvent gave a molecular weight of 1318 plus or minus 85. Methylated tannins in comparison, by Rast's method, gave a molecular weight of 1084 at low concentration and 1059 at higher. The same methylated tannin by Menzies-Wright ebullioscopic method gave molecular weights from 1190 to 1223 for lead-salt purified methylated tannins and 1123 to 1140 for acetone extracted methylated tannins. This indicates that methylated tannins and a non-polar solvent, such as benzene, are suitable for molecular weight determinations by different methods. The above molecular weights correspond to a value of 950 for tannin itself. The cryoscopic constant of benzene is 5.0. Bromoform with a cryoscopic constant of 14.2 and a convenient freezing point (8°C.) would be more suitable. The method of treatment of tannins as well as the method of formation of derivatives may have an effect on the result obtained. Some of the assumptions which have been made regarding the relationship of molecular weight to astringency, semi-colloidal nature, etc., require careful examination as other explanations than those given are possible. R. H. T.

Tannins V. The Fractionation of Quebracho Extract. By K. S. Kirby, E. Knowles and T. White. *J. Soc. Leather Trades' Chemists*, **37**, 283 (1953). The work of other investigators is discussed briefly. The experimental work is described in a special section. Solvent fractionation, which is carried out in a manner similar to that previously described for black wattle is summarized in the following schematic presentation and table:



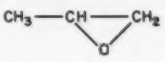
The fractions showed different tannin analyses and pH values (Table I) :—

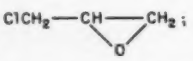
TABLE I.

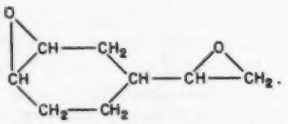
Fraction	Tans	Non-Tans	Insolubles	pH Analytical solution	pH 1% solution in 20% $MeOCH_2CH_2OH$
Q_{111}	90·2	9·1	0·7	3·6	3·7
Q_{112}	95·2	4·8	0·0	4·3	4·35
Q_{121}	86·0	3·3	10·7	4·0	4·1
Q_{122}	58·2	5·35	36·45	4·7	5·2
Q_{21}	63·0	16·5	20·5	4·75	5·25
Q_{22}	31·4	47·7	20·9	6·70	7·4

The ultra-violet absorption spectra of the total extract and each fraction were measured in the range 210-400 mμ in 50 per cent methanol-water. The curve of the extract is shown and the curves of the fractions are said to be similar. All show a maximum at 280-281 mμ indicative of phenolic nuclei. Paper chromatography is carried out as in a previous paper [*J. Soc. Leather Trades' Chemists*, **36**, 45 (1952). *This Jour.* **47**, 578 (1952)], except that mixed ferric chloride/potassium ferricyanide solutions were used in detecting the phenolic substances in addition to bis-diazotized benzidine. Application of this technique to the whole extract, and to fractions Q_{111}, Q_{112}, Q_{121}, Q_{122}, Q_{21} and Q_{22}, demonstrates the presence of 17 main substances (or complexes) and 23 minor substances in addition to at least 21 substances which fluoresce under ultra-violet light. Distributions and photographs of the chromatograms are given. R. H. T.

Studies on the Reactive Groups of Collagen. Part III. Cross-linkage and Its Relation to Tanning. By R. L. Sykes. *J. Soc. Leather Trades' Chemists*, **37**, 294 (1953). The present work deals with the effect of the acetates of mercury, zinc and cadmium, as one group, and of the 1, 2-epoxides as another. Both groups are claimed to introduce cross-linkages in proteins. Collagen was "tanned" with .2 *M* mercuric acetate in the presence of acetate buffer at four different initial pH values. At varying intervals, from five minutes to seven days, the pH of the solutions and the shrinkage temperature of the collagen were

taken. Similar runs were made with the acetates of cadmium and zinc. A like series was run with three epoxides, the monofunctional propylene oxide, 

epichlorhydrin with epoxy group and one chlorine, 

and 1-vinyl, 4 cyclohexane with two epoxide groups, 

The latter two compounds, being insoluble in water, were dissolved in 25 per cent ethanol. In all experiments the pelt was agitated throughout the reaction. The shrinkage temperature was taken in a specially designed apparatus which is described. All the acetates were most effective in the less acidic solutions, near the precipitation point. Meruric acetate was far more effective than the other two, giving a shrinkage temperature of 94°C. in 5 min. This product was stable to washing and imputrescible. In short it was leather. Propylene oxide had practically no effect. Epichlorhydrin had no effect in acid solution but in alkaline solution showed a shrinkage temperature increase comparable to that attained with aldehydes. A check experiment with deaminized pelt, by failure to increase the shrinkage temperature, indicated that this cross linking involved the amino groups. The cross linking of the diepoxy compound appeared to be independent of the pH. Although the shrinkage temperature of the treated collagen was not high (72°C.), the bonds introduced were exceptionally stable. It is suggested that the evidence presented favors the theory of tanning involving stable cross-linkages between adjacent polypeptide chains. R. H. T.

The Action of Large Ions on Collagen and Gelatin. By K. G. A. Pankhurst. *J. Soc. Leather Trades' Chemists*, **37**, 312 (1953). The over-all effect of any ion, whether it be large or small, has been shown to depend on (1) the extent to which it has been adsorbed on the protein, and (2) its degree of hydration. Highly hydrated ions not adsorbed by the protein tend to salt it out. Highly hydrated ions with a strong affinity for protein tend to solubilize it—salt it in. This paper is concerned with the action of detergents, which are partly hydrophilic and partly hydrophobic, on gelatin and collagen. A study using gelatin shows that a detergent of the nature of a hydrocarbon chain (oleophilic) with a polar end (hydrophilic) is first adsorbed with the polar head attached to the protein molecule, leaving the oleophilic chain outward. Thus the non-soluble chain at the interface makes the protein insoluble and it is precipitated. This takes place when the protein is completely covered with a monolayer of the detergent. It is called the "primary adsorption". If more detergent is added, a second layer is attached with the oleophilic side chains bound together by van der Waal's forces leaving the polar heads out. These, being hydrophilic, bring about the solution of the protein again. This is termed "secondary adsorption". A figure is given illustrating these two kinds of adsorption. The amount of detergent required for a monolayer (the primary adsorption) can be determined quantitatively. It is reduced if the protein is deaminized. The amount of detergent used for primary bonding may thus be used for determination of basic groups. If a cationic detergent is used, the ionized aspartic and glutamic acid may be determined in a like manner, although hydrolysis of the protein may introduce error. The stoichiometric binding of the

first layer is only found if inorganic electrolytes are absent. Salts increase the binding. Ammonium nitrate in molar concentration, for example, increases the binding about 4½ times. The binding increases with the inorganic electrolyte concentration. Besides increasing binding, inorganic salt makes possible the preciptation and coacervation at the isoelectric point. Data are given to support the belief that, in the presence of salt, there is an ion-dipole association with the keto-imide "backbone" groups of the gelatin. Viscosity studies show that, as detergent is added, viscosity decreases to a minimum and then increases. Minimum viscosity corresponds to the point of complete monolayer. The behavior of detergents with collagen is similar to that with gelatin although the structured nature of collagen may restrict the extent of their action. It has previously been shown that detergent anions produce a lowering of the shrinkage temperature of collagen. It was found in this work that detergents with less than 8 carbon chain length had little effect; but beyond that chain length there was a marked lowering which increased with increase of chain length. Analysis indicates that about one in fifty of the backbone keto-imide groups was involved. Applying the information derived from this work, it is difficult to see how detergents would improve soaking. The monolayer adsorption would cover the protein with a hydrophobic layer which would tend to hinder the soaking. To bring to the hydrophilic condition would require detergent, of the nature of dodecyl sodium sulfate, about 6 per cent of the weight of the skin. Of course, if the surface of the skin is greasy, a detergent would assist in grease dispersal. For degreasing pickled hides, anions are not very useful; but cations and non-ionics are fairly successful. Anions are ideal additions in paraffin degreasing. Sulfated oils used in fatliquoring are similar to anionic detergents, and behave similarly. Detergents can be used to assist dyeing in one of two ways. By using a detergent of the same electrical charge as the dye (anionic detergent with an acid dye) the dyeing process can be slowed and paler, more level shades produced. Pretreatment of the leather with a detergent of opposite charge (a cationic detergent with an acid dye) causes an intensification of the dye in the surface layers, thereby making it possible to simulate brush dyeing in a drum. R. H. T.

The Constitution of Sulfated Oils. V.—Effects of Variations of Preparation on the Composition of Sulfated Oleic Acid. By D. Burton and L. F. Byrne. *J. Soc. Leather Trades' Chemists*, **37**, 321 (1953). The history of oil sulfation is reviewed. The objective of this work was to study the effects of varying the conditions in sulfation of oleic acid. The plan of study is given in Table I, and the results in Table II.

TABLE I.
PLAN OF STUDY

37.5% H_2SO_4 for 3 hrs.	37.5% H_2SO_4 for 3 hrs.	20% H_2SO_4 for 3 hrs.		39% Chlorsulfonic acid plus 20% Glacial Acetic Acid for 4 hrs.
At 20°C	At 50°C	At 20°C		At 20°C
Washed with water at 20°C	Washed with 20% NaCl at 20°C	Washed with 20% NaCl at 20°C	Washed with 20% Na_2SO_4 at 20°C	Washed with 20% Na_2SO_4 at 20°C
Neutralized with caustic soda at 20°C	Neutralized with caustic soda at 20°C	Neutralized with caustic soda at 20°C	Neutralized with caustic soda at 20°C	Neutralized with caustic soda at 20°C
Oil I.	Oil II.	Oil III.	Oil IV.	Oil VI.
			Neutralized with ammonia at 20°C	
			Oil V.	

TABLE II.

Gm. Equiv. in the Sulfated Product Yielded by 100 g. Equiv. of Oleic Acid.

Oil No.	I	II	III	IV	V	VI
pH of 1% emulsion	4.65	4.65	6.55	4.7	4.85	6.3
—COOH (a)	89.9	90.8	52.2	96.7	102.1	40.7
—COONa (e) + —COONH$_4$ (f)	4.5	3.4	8.5	5.35	5.6	35.5
Lactones, Lactides and Estolides	7.9	8.1	42.6	0.25	5.4	26.1
—OSO$_2$O Na (g) + —OSO$_2$ ONH$_4$ (h)	37.8	33.0	0.0	23.9	24.1	18.6
—SO$_2$Na (i) + SO$_2$NH$_4$ (j)	0.8	1.1	3.6	0.0	0.0	12.9
Na$_2$SO$_4$ (k) + (NH$_4$)$_2$ SO$_4$ (m)—Grav. method	21.1	4.2	1.9	11.8	10.7	—
Na$_2$SO$_4$ (k) + (NH$_4$)$_2$ SO$_4$ (m)—Vol. method	—	—	2.2	—	—	33.5
Total Ammonia	0.0	0.0	0.0	0.0	20.6	0.0
Free and Neutralized Hydroxy Fatty Acids and their Derivatives (calc. from fall in Iodine Value	27.7	35.5	59.1	9.8	9.85	40.55
Fall in Iodine Value	132.7	139.7	143.5	67.4	67.9	144.1
Free and Neutralized Hydroxy Fatty Acids (calc. from fall in iodine and acid values)	19.8	27.4	16.5	9.55	—	14.45

Other investigators have failed to obtain a sulfated oleic acid with zero iodine value. An attempt to accomplish it in this work also failed. The data obtained are discussed fully and comparisons made with data obtained by Riess in his investigations. R. H. T.

A Comparison of "White Spirit" and "Paraffin" for Degreasing Sheepskins for Chrome Gloving Leather. By R. G. Mitton and K. G. A. Pankhurst. *J. Soc. Leather Trades' Chemists*, **37**, 331 (1953). In solvent degreasing there should be efficient grease removal, recovery of most of the solvent used and a grease, free from solvent contamination, produced for marketing. Many solvents are unsuitable because of toxicity and/or inflammability. In view of the narrower boiling range of "white spirit" as compared to the "paraffin" and the fact that a solvent similar to "white spirit", namely: Stoddard's Solvent, is being used for pre-tanning degreasing in the U. S., it seemed worth while to make a comparative study of these solvents. The solvents actually used were pool burning oil and pool vaporizing oil, for the paraffin oils; and pool white spirit, special white spirit (low aromatics) and special white spirit (high aromatics) for the white spirits. In two tanneries Persian sheepskins for gloving leather were degreased in the pickled state with these solvents. From the data obtained it appears that there is little to choose between the five solvents as regards efficiency of degreasing and quality of leather. However the grease and solvent recovery is greatly facilitated by the use of the lower boiling solvents, the white spirits. Grease recovered from the "paraffin oils" was always dark in color and heavily contaminated with solvents, which gave it, among other things, a very unpleasant odor. A yellow solid or semi-solid grease could be recovered from the spent pool white spirit and low aromatic white spirit, provided heating was reduced to a minimum during recovery.

R. H. T.

Rapid Analysis of Packinghouse Wastes. By K. A. Hirlinger and G. E. Gross. *Sewage and Ind. Wastes*, **25**, 958 (1953). Data sufficiently reliable for good plant control and for estimating the probable effect of discharged wastes on the receiving stream can be obtained the same day the sample is taken. Entirely satisfactory results can be had on a routine basis using the rapid methods evaluated in this paper. Data from the Kjeldahl nitrogen analysis and the Smith-Sanderson grease analysis will give a reliable check on grease and nitrogen losses from the plant. These same data can be used to calculate oxygen

demand. Use of these data (which can be easily confirmed by the reflux chromatic oxygen consumed analysis) will give the basis for a constant estimate of the probable effect of the sewage on the oxygen resources of the receiving stream. All of this information will be available rapidly enough to permit immediate corrective action whenever trouble develops.
J. F. W.

Charting a Course for the Future of Stream Pollution Control. By K. S. Watson. *Water & Sewage Works*, **100**, 421 (1953). Improvement is needed in the following areas of pollution control: 1. Industrial plants should give more consideration to control of the entire water cycle from influent to effluent. 2. Industrial plants and consulting engineering firms should develop or employ more personnel schooled in defining and reducing an industrial waste problem by within-the-plant, short-of-treatment steps. 3. Much more analytical information covering actual stream conditions all over the country is necessary. 4. Better methods for determining when a stream is polluted are quite important to evaluate the effects of polluting materials on the human system and aquatic life, if the clean stream efforts are to proceed on a completely sound and orderly basis. 5. Improved instruments and instrumentation would be of great help in defining stream and effluent conditions. 6. Instrumentation which will more fully proportion the feed of chemicals to the concentration of impurities requiring treatment will be an asset in almost every branch of the industrial waste treatment field. 7. Modification and redesign of many of the major items of equipment used in water and sewage treatment, to better serve the waste treatment field, should expedite progress in this area of operation. 8. Streamlining of the coliform determination as applied to pollution control, or the development of a more rapid procedure using a different organism, should simplify pollution abatement work. 9. Mature consideration is warranted by the question, are young men entering the pollution control field today equipped by the best educational background available to cope with the many problems which it presents.
J. F. W.

Salting Tests of Calf Skins in the Presence of Antiseptics. Year 1951. H. Vourloud and G. Desjours. *Bull. Assoc. Franc. Chimistes Inds. Cuir* **14**, 133 (1952). Tests were made with 14 lots of 8 skins each. Variables included: (a) washing before salting, (b) length of draining period before bundling (8 or 15 days), and (c) addition of antiseptics to the wash water or to the salt. After draining, the skins were bundled by fours, and stored about 4 months. The skins were examined after storage, after soaking, after unhairing, after tanning, and off frames. Each skin was graded by a point system, according to number of curing defects (salt stains, discoloration, heat, etc.). Results showed that the use of antiseptics improved the appearance of the cured skin, but this improvement was not apparent when the skins were examined in work. However all antiseptics reduced the incidence of salt stains, though none eliminated salt stains completely. Drainage for 15 days before bundling gave better results than drainage for 8 days. The outside skins of the bundles showed the most marked grain defects. These tests were made with salt denatured with naphthalene without added Na_2CO_3. The antiseptics tested were 2-naphthol, parachlormetacresol, "S54", Merpin, "acryptogene", and "cequartyl". *Examination of Finished Skins Prepared by Starting with the Salting Tests of May, 1951. ibid.* 147–52. The finished leather lots from the above tests were ranked according to a point system, taking into consideration the preservation of grain and flesh, and also the general characteristics of the leather. Skins that had been cured in the presence of parachlormetacresol, 2-naphthol, or "S54" were ranked highest, and skins cured without any antiseptic were ranked lowest. Merpin, "cequartyl" and "acryptogene" were relatively ineffective.
H. B. M.

Salting Tests on Calf Skins. P. Chambard. *ibid.* **14,** 152 (1952); see preceding abstract. Results of the foregoing salting tests are discussed. Use of antiseptics improves curing to some extent, but observance of proper salting conditions is more important. Antiseptic compounds are fixed by the proteins of the skin, thus depleting the interfibrillary brine, and permitting bacteria to multiply therein. The alleged beneficial effect of adding Na_2CO_3 to curing salt may be due to diminished fixation of antiseptics by skin. Pieces of skin were salted with 40% salt (normal) and 25% salt (low), with or without the addition of 2% Na_2CO_3 on the salt weight. In each series 2-naphthol was added in amounts varying from 0 to 5% of the salt. Bacterial counts were made on solutions prepared by agitating the skin with 2.5 parts of water for 1 hr., after curing for 15 days. For pieces cured with insufficient salt, the counts varied from 60 to 462 million bacteria per gram of skin, and both Na_2CO_3 and 2-naphthol apparently *increased* the counts. For pieces cured with 40% salt, the counts were as follows:

% 2-naphthol	Bacteria per gram (in millions)	
	Without Na_2CO_3	With Na_2CO_3
None	20	16
0.25	7.5	11
2.0	3	4
5.0	2.8	1.9

H. B. M.

Drying of Tannin Residues (Loss in the Oven). A. Jamet. *Bull. Assoc. Franc. Chimistes Inds. Cuir.* **14,** 137 (1952); see *ibid.* **11,** 160 (1949). Boynton (see *This Jour.* **47,** 298 (1952)) found that residue weights obtained in the Jamet oven (a steam-heated chamber through which is passed a current of air predried with silica gel) agreed with the weights obtained in the conventional drier for most extracts, but not for myrobalans, alagrobilla, or lignosulfonate extracts. The author finds that myrobalans residues lose weight continuously in the J. oven up to 90 minutes, but also lose weight in the conventional oven up to 7.5 hours. This is attributed to decomposition rather than to expulsion of H_2O. *Quantitative Tannin Analysis. The Drying of Analytical Tannin Residues. ibid.* 170-7. Chestnut and myrobalans residues, after evaporation of liquid, were dried in the Jamet oven for 4-24 minutes (chestnut) or 5-90 minutes (myrobalans), and in the conventional steam oven for 0.5-8 hours. For chestnut the residues reached constant weight in 4 minutes in the J. oven and in 1 hour in the conventional oven. Myrobalans residues reached constant weight (within 1 mg.) in 30 minutes in the J. oven, and lost weight continuously in the conventional oven up to 7.5 hours. The loss in weight between 1 and 7.5 hours was about 7 mg. Chestnut residues dried 4 min. in the J. oven lost a further 2 mg. in 15 hours in an electric oven (99-100°C.) while myrobalans residues dried 8 hours in the conventional oven lost a further 5 mg. in 15 hours in the electric oven. When these residues were redissolved, evaporated, and redried for 5 min. in the J. oven (chestnut) and 3 hours in the conventional oven (myrobalans), the residue weights were the same as those found after the 15 hour drying in the electric oven, indicating that the material expelled during the prolonged drying is not water. Myrobalans are decomposed by heat in the presence of H_2O; the % tannin found when myrobalans are dissolved at 100° is 2-3% lower than when it is dissolved at 70°. The continuous loss in weight of myrobalans in the con-

ventional oven, is attributed to the presence of H_2O vapor, which is absent from the J. oven. Small irregularities in weights of chestnut residues, dried up to 8 hours in the conventional oven, are shown to be caused by variations in atmospheric humidity,—a variable that is eliminated in the J. oven. H. B. M.

Tanning with the Tannin of the Bark of Eucalyptus Sideroxylon. P. Chambard and I. Jullien. *Bull. Assoc. Franc. Chimistes Inds. Cuir* **14,** 158 (1952); cf. *This Jour.* **48,** 445 (1953). Two decolorized eucalyptus extracts were prepared: (*A*) by treatment with $NaHSO_3$, HCOONa and HCOOH, and (*B*) same, after blending with 15% of a syntan (Albatan). Neither product was satisfactory alone; penetration was slow, and the leather did not have a good appearance. Tests were then made on blends of *A* and *B* with sweetened chestnut. Tannage with a 1:1 mixture of *A* and sweetened chestnut was unsatisfactory because the composition of the liquors changed after repeated use owing to selective take-up of chestnut. This was corrected by varying the proportions of *A* and chestnut added to the different vats, but this rather complex system required frequent and delicate control, and only 30% of the chestnut could be replaced by *A*. Better results were obtained with mixtures of sweetened chestnut with *B*. Satisfactory leathers were produced using 50% eucalyptus, 42% chestnut, and 8% synthetic tannin. Water absorption coefficients of the experimental leathers varied with the subsequent loading process employed. There was no indication that either eucalyptus or the syntan increased the water absorption. Yield values were satisfactory. H. B. M.

Methods of Analysis of Zirconium Tanning Products and Zirconium Tanned Leathers. Ph. Grach. *Bull Assoc. Franc. Chimistes Inds. Cuirs* **14,** 178 (1952). The French Zr tanning compound ZT23 has the composition: active ZrO_2 23-25, active SO_3 22-24, insoluble SiO_2 10-12, Na_2SO_4 33-34, H_2O (loss at 150°C.) 7-9%, basicity 30, pH (1% solution) 1.8-1.9. Only the basic Zr sulfate is an active tanning agent, but the SiO_2 plays a regulatory role. The chemistry, natural sources, and method of preparation of Zr compounds are reviewed briefly. The most important analytical determinations are ZrO_2, acid SO_3 and basicity. Occasional determinations of Fe, TiO_2, and soluble SiO_2 are advisable. These constituents generally amount to less than 0.2-1.0 and 0.6-0.8% respectively. The phosphate method for precipitating ZrO_2 is recommended. Mandelic acid precipitation works equally well, but the reagent is expensive. Both methods afford good separation from Fe and Ti in the amounts present. *Procedure:* Fuse 1-2 g. of finely ground sample with 10 g. $KHSO_4$. Dissolve in 200 ml. H_2O containing 10 ml. concentrated H_2SO_4. Heat, filter SiO_2, and wash with hot, aciduated H_2O. Collect filtrate and washings in a 500-ml. volumetric flask, add 30-40 ml. concentrated H_2SO_4, and make to volume (Solution A). The solution should be 4*N* in H_2SO_4. To 50-100 ml. of Solution A add slowly several ml. of H_2O_2, then a solution of $(NH_4)_3PO_4$ in an amount containing at least 2 g. dry $(NH_4)_3PO_4$. Heat for 2 hours at about 50°C. after adjusting the H_2SO_4 content to 3.7-4*N*. Filter. Wash first with cold 5% H_2SO_4 containing 2.5% $(NH_4)_3PO_4$, and then with cold 5% NH_4NO_3 till free from sulfate. Dry the precipitate at 110°C. and ignite first at a low temperature, gradually raised to 950-1000°C., preferably in an electric furnace. Desiccate and weigh. The ZrO_2 factor is 0.47 (theoretically 0.463). Determine TiO_2 and Fe colorimetrically in aliquots of Solution A. To determine acid SO_3 suspend 1-2 g. of finely ground sample in H_2O, boil, and add a slight excess of $BaCl_2$. Boil 3 minutes, add bromthymol blue or bromcresol purple indicator, titrate to the end point with *N* NaOH, add a 10% excess, and back-titrate with *N* acid. Calculate as H_2SO_4. Calculate Schorlemmer basicity. To determine soluble SiO_2 shake 35 g. of sample with 400 ml. H_2O, make to 500 ml., filter, add 10

ml. concentrated H_2SO_4 to 50 ml. filtrate, evaporate to fumes, take up the residue in water, filter, ignite and weigh as SiO_2. If desired determine total SiO_2 in the insoluble matter from the $KHSO_4$ fusion. To determine ZrO_2 in spent tanning liquors, evaporate a suitable volume, treated with H_2SO_4, to fumes, to destroy organic matter, make to volume, and proceed as above. For the mandelic acid method, fuse a 2-g. sample with $KHSO_4$, dissolve in dilute H_2SO_4, filter, and make to 250 ml. To 50 ml. add 20 ml. concentrated HCl and 50 ml. of a 16% solution of mandelic acid. Heat for 20 min. at 85°C. Filter and wash with a 5% mandelic acid solution containing 2% by volume of concentrated HCl. Ignite and weigh as ZrO_2. For Zr leathers, determine ZrO_2 in the leather ash. Determine SiO_2 in the insoluble matter from the $KHSO_4$ fusion of the ash. Determine total sulfate by the $BaSO_4$ method in a solution obtained by digesting 1 g. leather with 200 ml. of 0.05 *N* NH_4OH at the boiling point under reflux. There is no method for distinguishing acid from neutral sulfate in a Zr leather. For mixed Cr-Zr leather, determine Zr as above and determine Cr. in a Na_2CO_3 fusion of the ash of a separate sample. H. B. M.

Antiseptics and Germicides in the Leather Industry. Urbain J. Thuau. *Rev. Tech. Inds. Cuir.* **44,** 1, 23, 43, 63, 81, 101 (1952). This is a continuation of a serial article, the previous parts of which covered general properties of antiseptics and a discussion of what antiseptics are usable in the leather industry. These concluding installments contain the authors recommendations, as to use of antiseptics at different stages of leather manufacture. The author has a liking for phenyl Hg compounds, but has obtained good results with p-nitrophenol, 2-naphthol, and various familiar chlorinated phenolic compounds. For preserving raw skin, he advises raising the pH value to 10.5 or higher, by immersion in an alkaline bath before salting (or drying), and adding one of the above antiseptics (e.g. p-chloro-metacresol), either to the alkaline bath, or mixed with the salt, or sprayed on the salted skins. Use of $NaHF_2$ or Na_2SiF_6 is regarded with disfavor. For soaking green-salted skins he advises the use of Hg compounds or any of the common antiseptics, at pH = 8.5-9.5; for dried skin the pH should be 10 or higher. Use of an antiseptic bath for bated stock, after thorough rinsing, is advised. Antiseptics must be used with caution, if at all, in vegetable tanning, since some fermentations are desirable. Mold-preventive treatments for leather are discussed, and the necessity for adding antiseptics to pickle liquors, chrome liquors, and protein finishers is mentioned. H. B. M.

The Determination of the Isoelectric Point of Collagen. Influence of Swelling and of Tannage. A. Staib. *Bull. Assoc. Franc. Chimistes Inds. Cuir* **15,** 51 (1953): In the previous work a millivoltmeter was used to detect differential membrane potentials, and rather wide isoelectric zones were reported. By replacing the millivoltmeter by a potentiometer, precision was improved, and isoelectric points (IEP) were determined to ± 0.05 pH unit. An electro-osmotic method gave the same results. Curves are given for the pH value of collagen and of the external solution in the pH range 3.5-9.5, as functions of added acid or alkali. Below the IEP (6.4 in this case) collagen has a higher pH than the external solution; above the IEP, the reverse is true and the difference is less. Goat collagen (original IEP 4.70) was treated with various reagents for 6 or 25 days, then purified as previously described. IEP's after these treatments were: H_2O, 4.7; 0.2*N* NaOH, 4.4 (6 days), 4.0 (25 days); saturated $Ca(OH)_2$, 4.6 (6 days), 4.0 (25 days); 0.2*N* Na_2S, 5.0 (6 days), 5.8 2(5 days); 0.1*N* HCl, 6.0 (6 days). Thus NaOH and $Ca(OH)_2$ lowered IEP while Na_2S and HCl raised it. The following IEP's are reported for skins variously tanned and washed free from soluble ionogenic material: HCHO, 4.5; oil tannage, 4.1; quinone, 5.0; ZrO_2, 4.3; SiO_2, 4.7; Cr_2O_3, 7.8; untanned, 6.4. All the tannages except chrome lowered the IEP, indicating blockage of basic groups. H. B. M.

The Dewooling of Sheep Skins. P. Gourlay. *Rev. Tech. Inds. Cuir.* **44,** 26, 47, 67, (1952). The physical and chemical properties of wool are reviewed. Dewooling by the sweating process, by painting, and by enzyme action, is described. The enzyme process is considered very promising. H. B. M.

Iron Tannage in the Presence of Gluconic Acid. By P. Chambard and D. Martin. *Bull. Assoc. Franc. Chimistes Inds. Cuir.* **15,** 95 (1953). Tanning tests were made on pieces of bated skin. The liquors contained $Fe_2SO_4)_3$, gluconic acid, and Na_2CO_3 to give the desired basicity. Tannage was done with 200% liquor containing 7.5% Fe on the white weight, for 20 hrs., followed by rinsing (twice), neutralization with 200% of 0.1*N* $NaHCO_3$ (3 hrs.), 3 more rinsings, and drying. The leathers were analyzed for Fe_2O_3 and tested for shrink temperature (Ts) and percentage swelling. In the first series, using 0.2-1.0 mol gluconic acid per mol Fe, swelling increased and % Fe_2O_3 decreased progressively with increasing gluconic acid, and T_s was maximum (84°C.) for 0.3 mol gluconic acid. None of the leathers were satisfactory. In a second series, 0.4 mol gluconic acid was used throughout, and basicity was varied from 20 to 60 (before adding gluconic acid). This quantity of gluconic acid was the minimum necessary to stabilize the solutions at such basicities. With increasing basicity, % Fe_2O_3 n the leather increased, T_s increased, swelling decreased, and the character of the leather improved. Leathers tanned at 45 and at 60% basicity were considered satisfactory. The latter leather contained 12% Fe_2O_3, shrank at 96°C., and showed negligible swelling. H. B. M.

The Extracts of Chestnut and of Oak. P. Peureux. Conference Held at the Center for Improving Technique, November 5, 1952. Published by *Rev. Tech. Inds. Cuir* (separate pamphlet, 20pp.). A lecture discussing the effect of manufacturing conditions of chestnut and oak extracts on the quality of leather. Sorting, to eliminate too old and too young wood, branches, etc., magnetic removal of Fe, and mechanical screening to remove dirt, bark fragments, etc., result in improved color. Attempts to determine the maximum permissable Fe content have failed, because it depends on whether the Fe is present as inorganic salts or complexed with organic acids, and also on the $C\mu$ content, since the $C\mu$ increases the color due to Fe and vice versa. Temperature and time of extraction have a marked effect. The total tannin extracted increases with temperature and time, but simultaneously the purity and pH value are lowered and the color is impaired. Conditions should be regulated to give an extract of maximum purity and an acidity "just sufficient". Clarification, by sedimentation, removes tannins of high molecular weight, resulting in better penetration and improved color. Sedimentation is done preferably at a concentration of about 6° Baume, where insoluble matter is maximum, and at low temperature. The improvement by clarification may be undone by subsequent floculation during use, by the presence of Ca or Mg salts, or by the action of molds. Concentration and drying should be done at the minimum temperature and in the minimum time, to avoid a decrease in degree of dispersion and an impairment of color. Spray-dried extract always gives a better color than a comparable extract dried in the Kestner apparatus. The principles employed in producing "sweetened" (mellowed) extract are discussed. This involves raising the pH value of the extract, thereby rendering the extract less astringent. The degree of dispersion of the tannin is increased. The color of the extract, determined with the tintometer, is darkened, but the leather produced from mellowed extract has a clearer color. Preparation of mellowed extract must be done by adding the alkali slowly, to a dilute tannin solution, with rapid agitation. NaOH cannot be used. The agent actually used is not specified. Mellowed extracts have a lower purity because of their mineral matter content.

This is unimportant. Mellowed extract is more sensitive to heat, air and mold growth than normal chestnut. H. B. M.

Tanning Power and Chemical Constitution. P. Chambard. *Assoc. Franc. Chimistes Inds. Cuir,* Conference No. 10, Dec. 3, 1951 (18pp.). An address. No one mechanism can explain all tannages. Tannage may take place by ionic combination between positively charged amino-groups and anions of syntans, silcic acid, metaphosphoric acid, or chromic acid; by neutralization of oppositely charged colloids (similar to the foregoing since the charges are the result of ionization); by penetration of carboxyl or amino-groups of collagen into Cr, Fe, or Zr complexes; or by intermolecular action of aldehydes with amino-groups. Vegetable tannage results from mutual neutralization of charges, followed by reaction between phenolic groups and amino-groups. Combination of collagen with another material is not a sufficient condition for producing leather; the molecular size and hydrophobic character of the tanning agent are also important. Alum tannage is considered to be nothing more than a pickling. Oil tannage is a form of aldehyde tannage. H. B. M.

Specifications Concerning Leathers for Shoes Bearing the Quality Label of the (French) National Leather Council. Consulting Committee for Technical Research in the Leather Industry (Paul Chambard, Chairman). *Doc. Sci. Tech. Inst. Recherches Inds. Cuir.* January 1953, 26pp. The following specifications are proposed:

Type	Sole Leathers		Insoles
Chemical Analysis:	Work shoe and street shoe	Flexible soles for cemented shoes	
Greases[a]	No maximum; content reported		3-6
Water solubles (max.)[b]	18	18	14
Total ash (max.)[b]	2	2	4
$MgSO_4 \cdot 7H_2O$ (max)[b]	3	3	1
Soluble ash (max.)[b]	—	—	1
Insoluble ash	—	—	(c)
pH value (H_2O solubles solution) (min.)	3.5	3.5	3.5
Difference figure[d]	0.7	0.7	0.7
Physical tests: Water absorption in 24 hrs. (max.)	45	50	—
Water absorption in 1 hr. (min.)	—	—	25
Overall coefficient (min).	2	—	—
Softening by wetting (difference between dry and wet compressibility) (max.)	27.5	27.5	27.5
Wear resistance (compared to aluminum plate) (min.)	0.45	0.35	—
Tear resistance (kg. per mm. thickness)	—	—	3

Resistance to scuffing by knife point (kg. per mm. thickness) (min.)	—	—	11
Permeability to H_2O vapor (mg. H_2O per 10 cm^2. in 24 hrs.) (min.)	—	—	350

[a] on dry leather weight
[b] on dry, degreased leather weight
[c] to consist solely of lime and the constituents of kaolin and talc
[d] determined only if pH value is below 4.5

The "overall wetting index" is obtained by determining H_2O absorption in 1 hr. (corrected for thickness by a somewhat complicated formula), in 24 hours, and again in 24 hours after drying. A point scale, 0 to 5, is assigned to different ranges of percentages obtained in each of these tests (0 poorest), and the "overall index" is obtained by adding 0.4 of the points for each of the first 2 tests to 0.2 of the points for the last test. Determination of softening by wetting requires determination of hardness coefficient (thickness under compression of a cylinder 4 mm. in diameter, under a load of 70 kg., expressed as percentage of initial thickness) for dry leather and for leather soaked 24 hrs. The specifications are discussed and some data are given. Procedures for determining permeability to H_2O vapor, hardness coefficient, and water absorption are reprinted from wartime publications. H. B. M.

Leather Manufacture in Indonesia. By E. Gergely and A. H. Siregar. *Das Leder* **4**, 243 (1953). Indonesia has a warm, moist climate. There are two rice crops per year but all available land is planted in rice. There is no good grazing land for animals. Hide and skin production, in thousands, is as follows: cattle hides, 900; buffalo hides, 300; goatskins, 2000; sheepskins, 800; snakeskins, 230 and lizard skins, 130. Shoe production is as follows: all-leather shoes, 2 million pairs; sandals with at least leather uppers, 5 million pairs; and rubber-textile sandals, 4 million pairs. Most of the people are poor, 7 per cent are middle class and 1 per cent well off. State supported central plants (Induks) aid small companies in any way possible. They are collection points for hides and skins and tanning materials and also convert leather from small tanneries in their district into a higher quality product. Cattle hides from city and village slaughter houses are collected, usually by Chinese, dipped in a 0.5 per cent solution of arsenic trioxide then dried in the sun first with the hair side then the flesh side to the sun. The hair is short so the hides are transparent. They are not shorn as is done in some countries. The hump disappears during stretching and drying. 100 kilograms (kg.) of fresh or green hide yields 35 kg. of commercial dry hide. 1 kg. of dry hide is equivalent to 2.5 kg. of salted hide (salt free weight as determined in Europe). The hides are almost brand free and are not badly damaged by insects, scratches, etc. The principal damages are butcher cuts and poor cure. The cattle hides are light in weight and are classified as follows: up to 3 kg. (15 per cent of the total number of hides), 3-5 kg. (35 per cent), 5-7 kg. (30 per cent) and over 7 kg. (20 per cent). 1 kg. of the 3-5 class will yield 6 square feet (English) of leather. The classes of buffalo hides are 8, 8-10, 10-13, 13-15 and over 15 kg. Goatskins are dried without arsenic; 0.75 kg. of dry skin will yield 8 square feet of leather. They can be split to yield grains and chamois leather. Sheepskins have poor wool but the skins are good and sell for approximately the same as goatskins. High quality skins of lizards, various snakes, crocodiles and frogs are exported. The principal tanning materials are acacias and mangroves but there are many potential species on the different islands that have never been investigated. There are no extract plants. The strongest liquors used are 3°Bé liquors which

the tanner makes by leaching the tanning material with cold water. The leather is all tanned in Java by thousands of small tanneries using acacia. Goatskins are tanned, flesh out for lining and garment leather, etc., and buffalo hides for sole leather. Almost no machinery or power is available. The leather is dried in the sun. Sole leather is tanned in 4 weeks with acacia; penetration is rapid because the pH is 6.5 and the temperature about 27°C. The Djokdjakarta Institute is a school for practical leather manufacture which gives 3-month courses in tanning. I. D. C.

Hide Swelling in Chrome Tanning Solutions (making box calf from thin raw material). By A. Küntzel and F. Naumann. *Das Leder* **4**, 265 (1953). North German lowland cattle are kept for milk production. Calf skins from these animals are too thin, especially in the flanks, for shoe upper leather. Attempts to improve the leather by tanning in more highly masked chrome liquors or by retanning with vegetable tannin or syntan were not successful; the leather lost its box character and lacked firmness. Increased fullness could be obtained by increasing concentration or basicity of the tan liquor but only at the expense of sponginess, raw grain and dyeing trouble. An investigation was made of acid plumping during the early stages of tanning similar to that used in vegetable tanning. Only a very slight acid swelling is permissible in chrome tanning however. Swelling in a pickle is not satisfactory because acid alone will overswell the skin; salt depresses hydration below that of white hide; and regulation of the salt concentration to give moderate swelling is not practical because trivial amounts of salt cause large changes in swelling. An attempt was therefore made to regulate swelling in the tan liquor. For the experimental work acetone dehydrated white hide was used. It contained 15.4 per cent moisture, 0.49 per cent ash, 17.48 per cent nitrogen and rewet easily. For a test, 12 pieces of skin, weighing 1 ± .001 grams (air dry) were soaked in 10 cc. of water (soaked weight 2.45 ± 0.025 grams), then put into 8.55 cc. of tan liquor. This gave a ratio of skin to tan liquor of 1 to 10. After 24 hours the swollen skin was removed, drained 1 minute on a perforated plate, placed for 1 minute on filter paper—10 seconds with the split side to the paper then 50 seconds with the grain side to the paper—transferred to a weighing bottle and weighed to 1 milligram. The maximum deviation was 25 milligrams. To avoid a high neutral salt content, chromium sulfate solutions were prepared by reducing chromium trioxide with hydrogen peroxide at 0°-8°C. Chromium chloride solutions were made by dissolving $[CrCl_2(H_2O)_4]\ Cl \cdot 2H_2O$ "Merck". Each solution had a basicity of 0 per cent. Swelling (as measured by increase in weight) increased as chrome concentration increased to a maximum of about 0.5 grams per 2.45 grams of wet skin at a concentration of 20 grams chrome (Cr_2O_3) per liter. If the chrome liquor was boiled then cooled immediately before use, swelling was twice that caused by liquors prepared cold. Chromium chloride caused no swelling except for a slight swelling at very low concentrations. Studies of diffusion into 10 per cent gelatin gels showed that the hydrochloric acid (from hydrolysis) and the chromium chloride diffused into the gelatin at the same rate from chromium chloride solutions, whereas sulfuric acid diffused faster than chromium sulfate from chromium sulfate solutions. Swelling therefore occurred with the latter solution. A solution made 33 per cent basic by treating a 0 per cent basic chromium sulfate solution with barium hydroxide produced no noticeable swelling. The optimum volume of liquor (float) was 1000 per cent. Chrome alum can be used for swelling because the potassium sulfate it contains represses swelling noticeably only at higher concentrations. Practical tanning tests were made on calfskins, tanning the left sides by a standard method and the right sides with a swelling pretannage. A commercial chromium sulfate was used; it contained 4.7 per cent sodium sulfate and had a basicity of 23.6 but was made 0 basic with sulfuric acid. Optimum conditions for the pretannage were a liquor volume (float) of

1000 per cent based on dry collagen, and a chrome concentration of 12.5 grams Cr per liter in a 0 per cent basic chromium sulfate solution. As the bath was only half exhausted after use, lower concentrations were tried, but either a lower concentration at 1000 per cent float or less float at the optimum concentration resulted in decreased swelling. Increased swelling was obtained by boiling the chrome solution and cooling it just before use, but this swelling was accompanied by a decrease in area and poor tanning (shrinkage temperature, 85°C.) because plumping decreased penetration. Swelling retarded penetration in all cases but this effect was not important under optimum conditions. The liquor for the tanning proper should have a minimum concentration of 3.5 per cent Cr_2O_3 on the skin basis in order to obtain the desired fullness. Equally good results were obtained with a glucose reduced liquor or a commercial product (Chromosal S F) low in neutral salt. Skin tanned in the swollen condition requires more neutralization and 50 per cent more fat liquor than the usual tannage. This swelling resulted in a 15-25 per cent increase in thickness in the flanks and a 10-15 per cent increase in the bend but a 6-8 per cent loss in area. I. D. C.

Preparation of Hide Material for Swelling and Tanning Experiments. By F. Naumann. *Das Leder* **4**, 273 (1953). Tannin laboratories need a standard hide material corresponding to standard hide powder. It should be uniform and should not require long soaking to rewet it. Such a material can be prepared using a water miscible organic solvent and then drying with or without use of a water immiscible solvent such as xylol. This dry, "pseudo-leather" can be wet back to the white hide condition in an instant. Because of rapid evaporation of the solvent, however, atmospheric moisture is likely to condense on the collagen causing some glueing together of the fibers and making a product that is difficult to soak completely. Vacuum drying does not avoid this difficulty but covering the skin with filter paper during drying retards evaporation and cooling, and prevents moisture from reaching the skin. The method follows: Calfskin croupons were processed in the beam house as usual then split to equalize thickness. During bating they were well delimed. Pressing or centrifuging before dehydrating was advantageous. Dehydration with solvent was done in a 20 liter vessel. The cover, which was sealed with rubber and held by a clamp, was fitted with a manometer and a cock to relieve pressure. Progress of the dehydration was followed by testing with a hydrometer. The skin was rotated for 4-hour periods with 1.5 liter portions of acetone per kilogram of skin. Usually 3 changes of acetone were sufficient to reach a density of 0.798. The skin was then spread, grain down, on a glass table, set out on the split side, covered with filter paper and weighted with a lattice. The used acetone was recovered in a distilling column. The advantages of this material is that (a) it can be kept indefinitely in a tight container, (b) it can be determined by analyzing for moisture and nitrogen by usual methods, and (c) splitting or shaving is easier in the dry than in the wet condition. I. D. C.

The Damage to Pigskin Resulting from Scalding by the Dresden Scalding Process. By Fritz Stather. *Das Leder* **4**, 274 (1953). (See Hausam, *this Jour.* 48, 700). In a 3 year trial of the Dresden process, involving 6 million pieces of pigskin, 50 per cent of the skins were damaged so they could not be used for shoe upper leather. Hausam has ascribed defects in scalded skins to mechanical causes, but scalding may have made the skins tender and more easily damaged. His report shows that 16 per cent of the skins were at least partly damaged. Also the normal, comparison skins used by Hausam were scalded on the head and belly with water at 80°C, and had a gelatinized strip 10 centimeters wide along the belly edge of the croupon.

To further test the Dresden process, the following three sets of experiments were performed: (A) hogs weighing 100-120 kilograms (kg.) were scalded for 4, 5, 6, 7 or 10 minute periods at 60°C; (B) hogs weighing 100-120 kg. were scalded 6 minutes at temperatures of 57°, 60°, 62° or 65° respectively; and (C) hogs of 3 weight classes—80-100 kg., 100-120 kg., and 120-140 kg.—were scalded for 6 minutes at 60°C. Half of the croupon (bend) portion of the skin was removed immediately after bleeding, then the hog was scalded by one of the above methods, after which the remaining half croupon was removed. The two pieces of skin were cooled, sheared then used in comparative tests. The hair was not loosened sufficiently in either 4 or 5 minutes at 60° or in 6 minutes at 57°. All pieces, even those given a short scald, were slightly rubbery and the damage increased with the time and temperature of scalding. Leather made from skins scalded at 65° had the characteristic shredded grain of scald-damaged skins. Scalded skin had 10-23 per cent less tensile strength than unscalded skin. Leather from scalded skins had lower actual strength and tensile strength and was more than 10 per cent thinner than that from unscalded skins. When 100 gram portions of chopped skin were treated for 1 hour at 35°C with 1 per cent of tryptic enzyme, 50 per cent more nitrogen was found in solution from scalded than from unscalded skin. Scalding caused a lowering of fat and hide substance content but did not affect stretch or ash, or the chrome content of chrome tanned leather. To determine the area change caused by scalding, the areas of 4 freshly removed hog skins were measured, then the skins were scalded for 6 minutes at 4 different temperatures and the areas remeasured. The loss in area at 57° was 1.1 per cent; at 60°, 5.9 per cent; at 62°, 15.3 per cent; and at 65°, 6.5 per cent. The author concludes that scalding blood-warm hogs under conditions of the Dresden process (4-6 minutes at 59-62°) even with careful operation causes considerable damage which at times can not be recognized externally either on the raw hide or the finished leather. This damage is made evident by a lower hide substance content, an increased attack by tryptic enzymes, and an appreciably lower strength of the raw, limed, bated or tanned skin; further in a considerable decrease in thickness, greater softness, changed grain properties and lower wetability and air permeability of the leather. These facts support the unfavorable results of the leather industry with the Dresden scalding process. Treatment of skin with water at a temperature above 55°C must be avoided. I. D. C.

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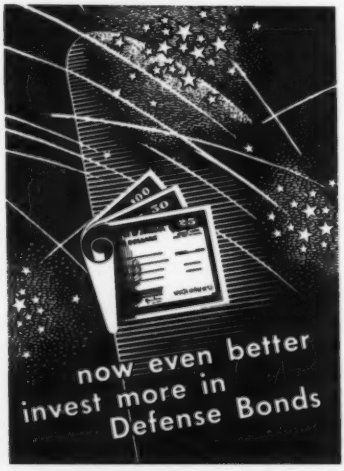

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